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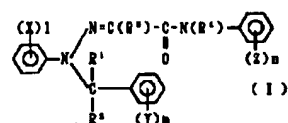
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(21)出願番号	特願平3-329518	(71)出願人	000232623 日本農薬株式会社 東京都中央区日本橋1丁目2番5号
(22)出願日	平成3年(1991)11月18日	(72)発明者	日野 智和 大阪府茨木市上穂積1丁目2-27
(31)優先権主張番号	特願平2-312414	(72)発明者	安藤 亘治 大阪府茨木市上穂積1丁目2-27
(32)優先日	平2(1990)11月17日	(72)発明者	濱口 洋 京都府京都市伏見区深草堀田町10-1、A-804
(33)優先権主張国	日本(J P)	(72)発明者	金岡 淳 大阪府河内長野市南花台3-3-24-110
		(74)代理人	弁理士 萆 経夫 (外2名)

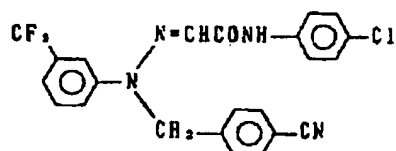
(54)【発明の名称】 ヒドラゾン誘導体及びその製造方法、その用途並びにその使用方法

(57)【要約】 (修正有)

【構成】 次式 (I)



具体的には、例えば

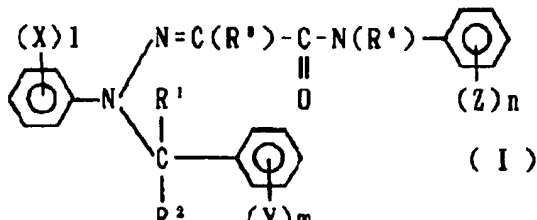


で示される化合物、その製法及び該化合物を有効成分とする農園芸用殺虫剤。

【効果】 優れた殺虫効果を示す。

【特許請求の範囲】

【請求項1】 一般式(I)



(式中、 R^1 、 R^2 、 R^3 及び NR^4 は同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xは同一又は異なっても良く、ハロゲン原子、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基又は低級アルキルスルホニル基を示し、Yは同一又は異なっても良く、ハロゲン原子、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルチオ基、低級ハロアルキルスルフィニル基、低級ハロアルキルスルホニル基、低級アルキニル基又は低級アルコキシカルボニル基を示し、Zは同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級ハロアルキルチオ基、低級アルキルスルフィニル基、低級ハロアルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルスルホニル基、低級アルキルカルボニル基又はフェノキシ

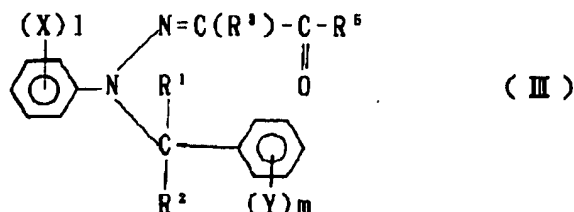
基を示し、1、m及びnは各々0～5の整数を示す。)で表されるヒドラゾン誘導体。

【請求項2】 一般式(I)において、 R^1 、 R^2 、 R^3 及び NR^4 が同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xが同一又は異なっても良く、ハロゲン原子、低級アルキル基、又は低級ハロアルキル基を示し、Yが同一又は異なっても良く、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級ハロアルキルチオ基又は低級ハロアルキルスルフィニル基を示し、Zが同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基又は低級ハロアルコキシ基を示し、1、m及びnが各々0～3の整数を示す請求項第1項記載のヒドラゾン誘導体。

【請求項3】 一般式(I)において、 R^1 、 R^2 、 R^3 及び NR^4 が同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xが同一又は異なっても良く、ハロゲン原子、低級アルキル基又は低級ハロアルキル基を示し、Yが同一又は異なっても良く、シアノ基、ニトロ基又は低級ハロアルキルスルフィニル基を示し、Zが同一又は異なっても良く、ハロゲン原子、低級ハロアルキル基又は低級ハロアルコキシ基を示し、1、m及びnが各々1～3の整数を示す請求項第2項記載のヒドラゾン誘導体。

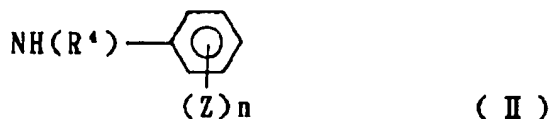
【請求項4】 一般式(I)において、少なくとも一個のXが3位に置換し、少なくとも一個のYが4位に置換し、少なくとも一個のZが4位に置換した請求項第3項記載のヒドラゾン誘導体。

【請求項5】 一般式(III)



(式中、 R^1 、 R^2 及び NR^3 は同一又は異なっても良く、水素原子又は低級アルキル基を示し、 R^5 はハロゲン原子又は水酸基を示し、Xは同一又は異なっても良く、ハロゲン原子、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基又は低級アルキルスルホニル基を示し、Yは同一又は異なっても良く、ハロゲン原子、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルチオ基、低級ハロアルキルスルフィニル基、低級ハロアルキルスルホニル基、低級アルキニル基又は低級アルコキシカルボニル基を示し、1及びmは各々0～5の整数を示す。)で表さ

れる化合物と一般式(II)



(式中、 R^4 は水素原子又は低級アルキル基を示し、Zは同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級ハロアルキルチオ基、低級アルキルスルフィニル基、低級ハロアルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルスルホニル基、低級ハロアルキルカルボニル基又はフェノキシ基を示し、nは0～5の整数を示す)

$$\begin{array}{c}
 \text{(X)}^1 \text{---} \text{C}_6\text{H}_4 \text{---} \text{N} \begin{cases} \text{---} \text{N}=\text{C}(\text{R}^3) \text{---} \text{C}(=\text{O}) \text{---} \text{N}(\text{R}^4) \text{---} \text{C}_6\text{H}_4 \text{---} \text{(Z)}^n \\ \text{---} \text{C}(\text{R}^1) \text{---} \text{C}_6\text{H}_4 \text{---} \text{(Y)}^m \\ \text{---} \text{C}(\text{R}^2) \end{cases}
 \end{array}
 \quad \text{(I)}$$
$$\text{Hal}-\underset{\text{R}^2}{\overset{\text{R}^1}{\text{C}}}-\text{C}_6\text{H}_4-\underset{\text{(Y)}_m}{\text{C}} \quad (\text{V})$$

(式中、 R^1 、 R^2 、 R^3 、 R^4 、 X 、 Y 、 Z 、 l 、 m 及び n は前記に同じ。)で表されるヒドラゾン誘導体の製造方法。

$$\text{C}-\text{N}(\text{R}')-\text{C}_6\text{H}_4-(Z)_n \quad (\text{IV})$$

【請求項7】 一般式(I)

$$\begin{array}{c}
 \text{(X)}_1 \text{---} \text{C}_6\text{H}_4 \text{---} \text{N} \begin{array}{l} \diagup \text{N}=\text{C}(\text{R}^3) \text{---} \text{C}(=\text{O}) \text{---} \text{N}(\text{R}^4) \text{---} \text{C}_6\text{H}_4 \text{---} (\text{Z})_n \\ \diagdown \text{R}^1 \\ | \\ \text{C} \text{---} \text{C}_6\text{H}_4 \text{---} (\text{Y})_m \\ | \\ \text{R}^2 \end{array} \\
 \text{(I)}
 \end{array}$$

-3-

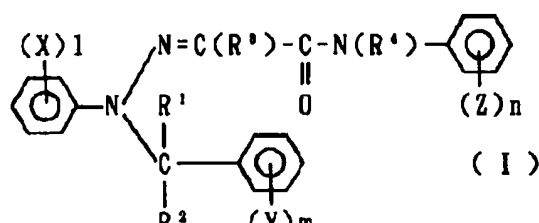
ハロアルキルスルホニル基、低級ハロアルキルスルホニルオキシ基、低級アルキルカルボニル基又はフェノキシ基を示し、1、m及びnは各々0～5の整数を示す。)で表されるヒドラゾン誘導体を有効成分として含有することを特徴とする農園芸用殺虫剤。

【請求項8】 一般式(I)において、 R^1 、 R^2 、 R^3 及び R^4 が同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xが同一又は異なっても良く、ハロゲン原子、低級アルキル基、又は低級ハロアルキル基を示し、Yが同一又は異なっても良く、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級ハロアルキルチオ基又は低級ハロアルキルスルフィニル基を示し、Zが同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基又は低級ハロアルコキシ基を示し、1、m及びnが各々0～3の整数を示す請求項第7項記載の農園芸用殺虫剤。

【請求項9】 一般式(I)において、 R^1 、 R^2 、 R^3 及び R^4 が同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xが同一又は異なっても良く、ハロゲン原子、低級アルキル基又は低級ハロアルキル基を示し、Yが同一又は異なっても良く、シアノ基、ニトロ基又は低級ハロアルキルスルフィニル基を示し、Zが同一又は異なっても良く、ハロゲン原子、低級ハロアルキル基又は低級ハロアルコキシ基を示し、1、m及びnが各々1～3の整数を示す請求項第8項記載の農園芸用殺虫剤。

【請求項10】 一般式(I)において、少なくとも一個のXが3位に置換し、少なくとも一個のYが4位に置換し、少なくとも一個のZが4位に置換している請求項第9項記載の農園芸用殺虫剤。

【請求項11】 有用作物を望ましからぬ害虫から防除するために一般式(I)



(式中、 R^1 、 R^2 、 R^3 及び R^4 は同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xは同一又は異なっても良く、ハロゲン原子、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基又は低級アルキルスルホニル基を示し、Yは同一又は異なっても良く、ハロゲン原子、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルチオ基、低級ハロアルキルスルフィニル基、低級ハ

ロアルキルスルホニル基、低級アルキニル基又は低級アルコキシカルボニル基を示し、Zは同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級ハロアルキルチオ基、低級アルキルスルフィニル基、低級ハロアルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルスルホニル基、低級ハロアルキルスルホニルオキシ基、低級アルキルカルボニル基又はフェノキシ基を示し、1、m及びnは各々0～5の整数を示す。)で表されるヒドラゾン誘導体を有効成分として含有する農園芸用殺虫剤を、有効成分として10アール当たり1g～5kgの薬量で処理することを特徴とする望ましからぬ害虫の防除方法。

【請求項12】 一般式(I)において、 R^1 、 R^2 、 R^3 及び R^4 が同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xが同一又は異なっても良く、ハロゲン原子、低級アルキル基、又は低級ハロアルキル基を示し、Yが同一又は異なっても良く、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級ハロアルキルチオ基又は低級ハロアルキルスルフィニル基を示し、Zが同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基又は低級ハロアルコキシ基を示し、1、m及びnが各々0～3の整数を示す請求項第11項記載の防除方法。

【請求項13】 一般式(I)において、 R^1 、 R^2 、 R^3 及び R^4 が同一又は異なっても良く、水素原子又は低級アルキル基を示し、Xが同一又は異なっても良く、ハロゲン原子、低級アルキル基又は低級ハロアルキル基を示し、Yが同一又は異なっても良く、シアノ基、ニトロ基又は低級ハロアルキルスルフィニル基を示し、Zが同一又は異なっても良く、ハロゲン原子、低級ハロアルキル基又は低級ハロアルコキシ基を示し、1、m及びnが各々1～3の整数を示す請求項第12項記載の防除方法。

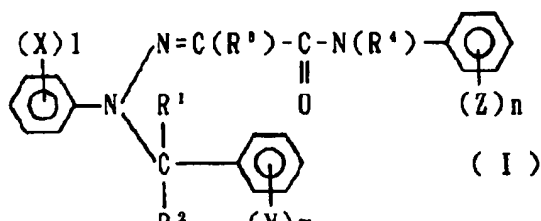
【請求項14】 一般式(I)において、少なくとも一個のXが3位に置換し、少なくとも一個のYが4位に置換し、少なくとも一個のZが4位に置換した請求項第13項記載の防除方法。

【請求項15】 害虫が鱗翅目害虫又は甲虫目害虫である請求項第14項記載の防除方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は一般式(I)



(式中、 R^1 、 R^2 、 R^3 及び R^4 は同一又は異なっても良く、水素原子又は低級アルキル基を示し、 X は同一又は異なっても良く、ハロゲン原子、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基又は低級アルキルスルホニル基を示し、 Y は同一又は異なっても良く、ハロゲン原子、シアノ基、ニトロ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級アルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルチオ基、低級ハロアルキルスルフィニル基、低級ハロアルキルスルホニル基、低級アルキニル基又は低級アルコキシカルボニル基を示し、 Z は同一又は異なっても良く、ハロゲン原子、ニトロ基、シアノ基、低級アルキル基、低級ハロアルキル基、低級アルコキシ基、低級ハロアルコキシ基、低級アルキルチオ基、低級ハロアルキ

ルチオ基、低級アルキルスルフィニル基、低級ハロアルキルスルフィニル基、低級アルキルスルホニル基、低級ハロアルキルスルホニル基、低級ハロアルキルスルホニルオキシ基、低級アルキルカルボニル基又はフェノキシ基を示し、 l 、 m 及び n は各々0～5の整数を示す。)で表されるヒドラゾン誘導体、その製造方法及び農園芸用殺虫剤並びにその使用方法に関するものである。

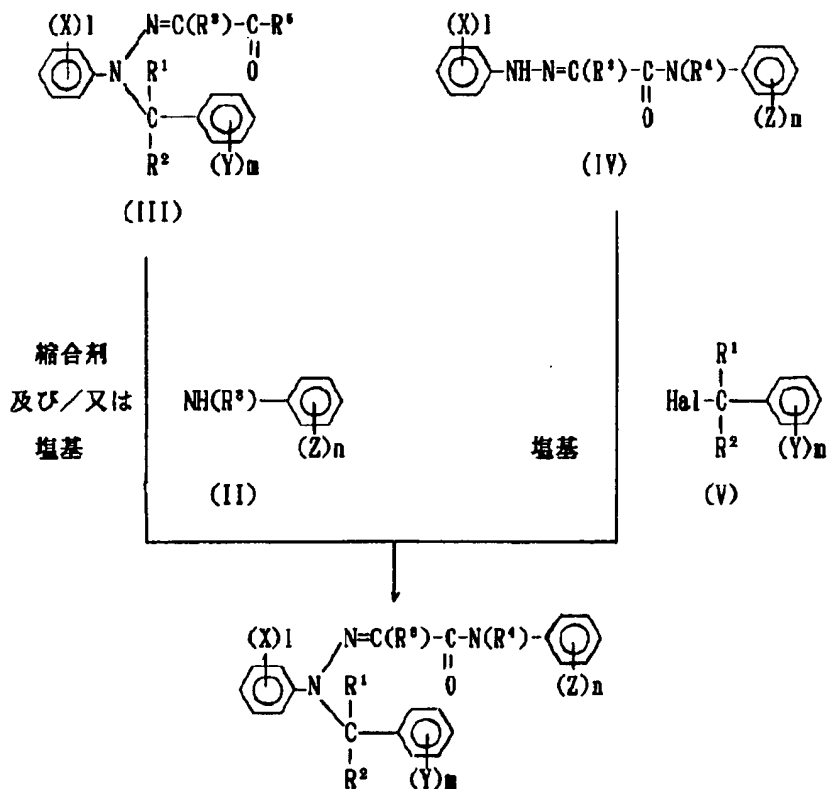
【0002】

【従来の技術】特開昭48-91223号、特開昭54-122261号、特開昭56-45452号、特開昭63-93761号公報等にヒドラゾン類が殺虫剤、有害生物防除剤として開示されている。

【発明が解決しようとする課題】本発明者等は新規な殺虫剤を創出すべく鋭意研究を重ねた結果、一般式(I)で表されるヒドラゾン誘導体が先行技術文献等に記載も示唆もされておらず、文献未記載の新規化合物であり、且つ低薬量で優れた殺虫効果を有することを見出し本発明を完成させたものである。

【0003】

【課題を解決するための手段】本発明の一般式(I)で表されるヒドラゾン誘導体の代表的な製造方法としては、例えば下記に図示する製造方法により製造することができる。



(式中、 R^1 、 R^2 、 R^3 、 R^4 、 R^5 、 X 、 Y 、 Z 、 l 、 m 及び n は前記に同じ。)

一般式(III)で表される化合物と一般式(II)で表されるアニリン類とを不活性溶媒の存在下、塩基及び又は縮合

剤の存在下又は不存在下に反応させるか、又は一般式(I)で表される化合物と一般式(V)で表されるハライド類とを不活性溶媒及び塩基の存在下に反応させることにより一般式(I)で表されるヒドラゾン誘導体を製造することができる。

【0004】1. 一般式(III) → 一般式(I)

本反応で使用できる不活性溶媒としては、本反応の進行を著しく阻害しないものであれば良く、例えばジクロロメタン、クロロホルム、四塩化炭素等のハロゲン化炭化水素類、ベンゼン、トルエン、キシレン等の芳香族炭化水素類、アセトニトリル、ベンゾニトリル等のニトリル類、メチルセロソルブ、ジエチルエーテル等の鎖状エーテル類、ジオキサン、テトラヒドロフラン等の環状エーテル類、アセトン、メチルエチルケトン等のケトン類、酢酸エチル等のエステル類、N, N-ジメチルホルムアミド (DMF)、ジメチルスルホキシド (DMSO)、ピリジン等を例示することができ、これらの不活性溶媒は単独で使用しても良く、混合して使用することもできる。本反応で使用する塩基としては有機塩基又は無機塩基を使用することができ、無機塩基としては、例えばナトリウム、カリウム等のアルカリ金属原子、カルシウム、マグネシウム等アルカリ土類金属原子の水酸化物又は炭酸塩等、水素化ナトリウム等のアルカリ金属原子の水素化物、有機塩基としてはトリエチルアミン、ピリジン、N, N-ジメチルアニリン、2, 6-ジメチルピリジン、4-N, N-ジメチルアミノピリジン等を使用することができ、その使用量は触媒量乃至一般式(III)で表される化合物に対して等モル乃至過剰モルの範囲から選択して使用することができる。

【0005】縮合剤としては、例えばカルボジイミダゾール、ジシクロヘキシルカルボジイミド、ヨウ化2-クロロ-1-メチルピリジニウム等を使用することができ、その使用量は一般式(III)で表される化合物に対して等モル乃至過剰モルの範囲から選択して使用すれば良い。本反応は等モル反応であるので、各反応剤を等モル使用すれば良いが、アニリン類を過剰に使用することもできる。反応温度は室温乃至使用する不活性溶媒の沸点域の範囲から適宜選択すれば良く、好ましくは加熱下に行うのが良い。反応時間は反応量、反応温度等により一定しないが、数分乃至48時間の範囲から選択すれば良い。反応終了後、目的物を含む反応液から常法、例えば溶媒留去、溶媒抽出等を行い、必要に応じて再結晶法、カラムクロマトグラフィー法等により精製することにより目的物を製造することができる。

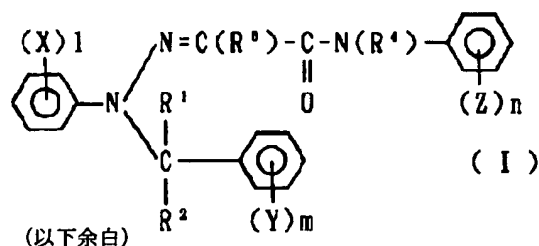
【0006】2. 一般式(IV) → 一般式(I)

一般式(IV)で表される化合物と一般式(V)で表されるハライド類とを不活性溶媒及び塩基の存在下に反応させることにより一般式(I)で表されるヒドラゾン誘導体を製造することができる。本反応で使用できる不活性溶媒としては、本反応の進行を著しく阻害しないものであれば

良く、例えばメタノール、エタノール、プロパノール等のアルコール類、ジクロロメタン、クロロホルム、四塩化炭素等のハロゲン化炭化水素類、ベンゼン、トルエン、キシレン等の芳香族炭化水素類、アセトニトリル、ベンゾニトリル等のニトリル類、メチルセロソルブ、ジエチルエーテル等の鎖状エーテル類、ジオキサン、テトラヒドロフラン等の環状エーテル類、アセトン等のケトン類、酢酸エチル等のエステル類、ジメチルホルムアミド、ジメチルアセトアミド、ジメチルスルホキシド、水等を例示することができ、これらの不活性溶媒は単独で使用しても良く、混合して使用することもできる。本反応で使用する塩基としては有機塩基又は無機塩基を使用することができ、無機塩基としては、例えばナトリウム、カリウム等のアルカリ金属原子、カルシウム、マグネシウム等アルカリ土類金属原子の水酸化物又は炭酸塩等、水素化ナトリウム等のアルカリ金属原子の水素化物、有機塩基としてはナトリウムメトキサイド、カリウムt-ブトキサイド等のアルカリ金属原子のアルコラート類、ナトリウムアミン等のアルカリ金属原子のアミノ化合物、トリエチルアミン等の三級アルキルアミン類、ピリジン、4-N, N-ジメチルアミノピリジン等を使用することができる。

【0007】塩基の使用量は一般式(IV)で表される化合物に対して等モル乃至過剰モルの範囲から選択して使用すれば良い。本反応は等モル反応であるので各反応剤を等モル使用すれば良いが、一般式(V)で表されるハライド類を過剰に使用することもできる。反応温度は室温乃至使用する不活性溶媒の沸点域の範囲から適宜選択すれば良い。反応時間は反応量、反応温度等により一定しないが、数分乃至48時間の範囲から選択すれば良い。反応終了後、前記の反応と同様にすることにより目的物を製造することができる。本発明の一般式(I)で表されるヒドラゾン誘導体を製造する際の原料化合物である一般式(III)で表される化合物は特開昭62-223169号、同64-70462号公報、J. Org. Chem., 417(1941)、Ber. 56B, 1060-1065(1923)等に記載の方法により製造することができる。又一般式(IV)で表される化合物は Collection Czech. Chem. Commun., 25, 2651-2667(1960)に記載の方法により製造することができる。以下に本発明の一般式(I)を第1表に例示するが、本発明はこれらの化合物に限定されるものではない。

【0008】一般式(I)



【表1】

第 1 表

No.	R ¹	R ²	R ³	R ⁴	(X)l	(Y)m	(Z)n	物 性
1	H	H	H	H	H	H	H	m. p. 172.1 °C
2	H	H	H	H	H	H	4-CH ₃	m. p. 155.2-152.9 °C
3	H	H	H	H	H	H	4-OCF ₃	m. p. 113.3-114.0 °C
4	H	H	H	H	H	4-Cl	4-CF ₃	m. p. 159.7 °C
5	H	H	H	H	H	4-Cl	4-OCF ₃	m. p. 137.8 °C
6	H	H	H	H	H	4-Cl	4-COCH ₃	m. p. 187.9 °C
7	H	H	H	H	H	4-CN	4-Cl	m. p. 163 °C
8	H	H	H	H	H	4-CN	4-CF ₃	m. p. 184-185 °C
9	H	H	H	H	H	4-CN	4-OCF ₃	m. p. 138 °C
10	H	H	H	H	H	4-CO ₂ CH ₃	4-OCF ₃	m. p. 159 °C
11	H	H	H	H	H	4-CO ₂ C ₂ H ₅ -t	4-OCF ₃	m. p. 142.2-143.7 °C
12	H	H	H	H	3-Cl	4-Cl	2-Cl	m. p. 135.5-137.0 °C
13	H	H	H	H	3-Cl	4-Cl	3-Cl	m. p. 130.3 °C
14	H	H	H	H	3-Cl	4-Cl	4-Cl	m. p. 143.5-144.0 °C
15	H	H	H	H	3-Cl	4-Cl	3-CH ₃	m. p. 128.5 °C
16	H	H	H	H	3-Cl	4-Cl	4-CH ₃	m. p. 149.6-150.0 °C
17	H	H	H	H	3-Cl	4-Cl	4-OCF ₃	m. p. 139.6-141.5 °C
18	H	H	H	H	3-Cl	4-NO ₂	4-Cl	m. p. 174.0-176.5 °C
19	H	H	H	H	3-Cl	4-NO ₂	4-OCF ₃	m. p. 151.6-151.7 °C
20	H	H	H	H	3-Cl	4-CN	4-Cl	m. p. 191.0-192.0 °C
21	H	H	H	H	3-Cl	4-CN	4-CF ₃	m. p. 202.9 °C


【表2】

第 1 表 (続 き)

No.	R ¹	R ²	R ³	R ⁴	(X) _l	(Y) _m	(Z) _n	物 性
22	H	H	H	H	3-Cl	4-CN	4-OCF ₃	m. p. 160.5-162.0 °C
23	H	H	H	H	3-Cl	4-CN	4-SCF ₃	m. p. 188.0 °C
24	H	H	H	H	3-Cl	4-CN	4-SOCF ₃	m. p. 206.1 °C
25	H	H	H	H	3-Cl	4-OCF ₃	4-CF ₃	m. p. 144 °C
26	H	H	H	H	3-Cl	4-OCF ₃	4-OCF ₃	m. p. 180-181 °C
27	H	H	H	H	4-Cl	4-NO ₂	4-Cl	m. p. 162.2 °C
28	H	H	H	H	4-Cl	4-NO ₂	4-OCF ₃	m. p. 111.0-115.1 °C
29	H	H	H	H	3-F	4-CN	4-Cl	m. p. 154-156 °C
30	H	H	H	H	3-F	4-CN	4-CF ₃	m. p. 178 °C
31	H	H	H	H	3-F	4-CN	4-OCF ₃	m. p. 155.9-156.8 °C
32	H	H	H	H	3-CH ₃	4-CN	4-Cl	m. p. 127 °C
33	H	H	H	H	3-CH ₃	4-CN	4-CF ₃	m. p. 153-155 °C
34	H	H	H	H	3-CH ₃	4-CN	4-OCF ₃	m. p. 166 °C
35	H	H	H	H	4-CH ₃	4-Cl	4-CF ₃	m. p. 167.9-169.5 °C
36	H	H	H	H	4-CH ₃	4-Cl	4-OCF ₃	m. p. 167.4 °C
37	H	H	H	H	4-CH ₃	4-CN	4-OCF ₃	m. p. 150.6-151.2 °C
38	H	H	H	H	3-CF ₃	4-CN	4-Cl	m. p. 164-165 °C
39	H	H	H	H	3-CF ₃	4-CN	4-F	m. p. 173-175 °C
40	H	H	H	H	3-CF ₃	4-CN	4-Br	m. p. 164 °C
41	H	H	H	H	3-CF ₃	4-CN	4-I	m. p. 80 °C
42	H	H	H	H	3-CF ₃	4-CN	4-CF ₃	m. p. 191.5-192.0 °C

【表 3】

第 1 表 (続き)

No.	R ¹	R ²	R ³	R ⁴	(X)l	(Y)m	(Z)n	物 性
43	H	H	H	H	3-CF ₃	4-CN	4-NO ₂	m. p. 236-238 °C
44	H	H	H	H	3-CF ₃	4-CN	4-CN	m. p. 174.5-175.1 °C
45	H	H	H	H	3-CF ₃	4-CN	3-CF ₃	m. p. 151.1-152.5 °C
46	H	H	H	H	3-CF ₃	4-CN	4-OCH ₃	m. p. 167 °C
47	H	H	H	H	3-CF ₃	4-CN	4-OCF ₃	m. p. 151.0 °C
48	H	H	H	H	3-CF ₃	4-CN	4-O- 	m. p. 156 °C
49	H	H	H	H	3-CF ₃	4-CN	2,4-Cl ₂	m. p. 78 °C
50	H	H	H	H	3-CF ₃	4-CN	3,4-Cl ₂	m. p. 213 °C
51	H	H	H	H	3-CF ₃	4-CN	3,5-Cl ₂	m. p. 169 °C
52	H	H	H	H	3-CF ₃	4-CN	3-Cl-4-F	m. p. 194 °C
53	H	H	H	H	3-CF ₃	4-CF ₃	4-CF ₃	m. p. 144.2 °C
54	H	H	H	H	3-CF ₃	4-CF ₃	4-OCF ₃	m. p. 142.6-144.7 °C
55	H	H	H	H	3-CF ₃	4-OCHF ₃	4-Cl	m. p. 124 °C
56	H	H	H	H	3-CF ₃	4-OCHF ₃	4-CF ₃	m. p. 108 °C
57	H	H	H	H	3-CF ₃	4-OCHF ₃	4-OCF ₃	m. p. 105-106 °C
58	H	H	H	H	3-CF ₃	4-SCH ₃	4-Cl	m. p. 146 °C
59	H	H	H	H	3-CF ₃	4-SCH ₃	4-OCF ₃	m. p. 134 °C
60	H	H	H	H	3-CF ₃	4-SOCH ₃	4-OCF ₃	m. p. 171 °C
61	H	H	H	H	3-CF ₃	4-SO ₂ CH ₃	4-OCF ₃	m. p. 193-194 °C
62	H	H	H	H	3,4-Cl ₂	4-CN	4-CF ₃	m. p. 224-231 °C
63	H	H	H	H	3,4-Cl ₂	4-CN	4-OCF ₃	m. p. 224.0 °C

【表 4】

第 1 表 (続 き)

No.	R ¹	R ²	R ³	R ⁴	(X) ₁	(Y) _m	(Z) _n	物 性
64	H	H	H	H	3,5-Cl ₂	4-CN	4-CF ₃	m. p. 255.5-258.0 °C
65	H	H	H	H	3,5-Cl ₂	4-CN	4-OCF ₃	m. p. 221.7-223.3 °C
66	H	CH ₃	H	H	4-Cl	4-Cl	4-Cl	ペースト状物
67	H	CH ₃	H	H	4-Cl	4-Cl	4-OCF ₃	ペースト状物
68	H	H	H	CH ₃	3-Cl	4-CN	4-OCF ₃	nD 1.5950(25 °C)
69	H	H	H	CH ₃	4-Cl	4-Cl	H	nD 1.6365(27°C)
70	H	H	H	CH ₃	4-Cl	4-Cl	4-Cl	ペースト状物
71	H	H	H	CH ₃	4-Cl	4-Cl	4-OCF ₃	nD 1.5939(27°C)
72	H	H	CH ₃	H	3-CF ₃	4-CN	4-Cl	m. p. 209-211 °C
73	H	H	CH ₃	H	3-CF ₃	4-CN	4-CF ₃	m. p. 181 °C
74	H	H	H	H	3-CF ₃	4-SO ₂ CH ₃	4-Cl	m. p. 228 °C
75	H	H	H	H	3-CF ₃	4-SOCH ₃	4-Cl	m. p. 178 °C
76	H	H	H	H	3-CF ₃	4-CN	4-OSO ₂ CF ₃	m. p. 172 °C
77	H	H	H	H	3-CF ₃	4-CN	4-OCF ₃ CHP ₂	m. p. 153 °C
78	H	H	H	H	3-CF ₃	4-SCHP ₂	4-OCF ₃	m. p. 134 °C
79	H	H	H	H	3-CF ₃	4-SCHP ₂	4-Cl	m. p. 143 °C
80	H	H	H	H	3-CF ₃	4-SCHP ₂	4-Br	m. p. 145 °C
81	H	H	H	H	3-CF ₃	4-SOCHP ₂	4-OCF ₃	m. p. 143 °C
82	H	H	H	H	3-CF ₃	4-SOCHP ₂	4-Cl	m. p. 181 °C
83	H	H	H	H	3-CF ₃	4-SOCHP ₂	4-Br	m. p. 171 °C
84	H	H	H	H	3-CF ₃	4-SO ₂ CHP ₂	4-OCF ₃	m. p. 109-110 °C

【表 5】

第 1 表 (続き)

No.	R ¹	R ²	R ³	R ⁴	(X) _l	(Y) _m	(Z) _n	物 性
85	H	H	H	H	3-CP ₂	4-SO ₂ CHP ₂	4-Cl	m. p. 222 °C
86	H	H	H	H	3-CP ₂	4-SO ₂ CHP ₂	4-Br	m. p. 213 °C
87	H	H	H	H	3-NO ₂	4-CN	4-OCF ₃	m. p. 190-191 °C
88	H	H	H	H	3-NO ₂	4-CN	4-CP ₂	m. p. 213-215 °C
89	H	H	H	H	3-NO ₂	4-CN	4-Cl	m. p. 205 °C
90	H	H	H	H	3-NO ₂	4-CN	4-Br	m. p. 215-217 °C
91	H	H	H	H	3-C ₂ H ₅	4-CN	4-OCF ₃	m. p. 157 °C
92	H	H	H	H	3-C ₂ H ₅	4-CN	4-CP ₂	m. p. 166 °C
93	H	H	H	H	3-C ₂ H ₅	4-CN	4-Cl	m. p. 142 °C
94	H	H	H	H	3-C ₂ H ₅	4-CN	4-Br	m. p. 133 °C
95	H	H	H	H	3-OCH ₃	4-CN	4-OCF ₃	m. p. 154 °C
96	H	H	H	H	3-OCH ₃	4-CN	4-CP ₂	m. p. 157 °C
97	H	H	H	H	3-OCH ₃	4-CN	4-Cl	m. p. 169 °C
98	H	H	H	H	3-OCH ₃	4-CN	4-Br	m. p. 153 °C
99	H	H	H	H	4-CH ₃	4-CN	4-OCF ₃	m. p. 170 °C
100	H	H	H	H	4-CH ₃	4-CN	4-CP ₂	m. p. 160 °C
101	H	H	H	H	4-CH ₃	4-CN	4-Cl	m. p. 158 °C
102	H	H	H	H	4-CH ₃	4-CN	4-Br	m. p. 178 °C
103	H	H	H	H	4-Cl	4-CN	4-OCF ₃	m. p. 158 °C
104	H	H	H	H	4-Cl	4-CN	4-CP ₂	m. p. 168 °C
105	H	H	H	H	4-Cl	4-CN	4-Cl	m. p. 211 °C

【表6】

第 1 表 (続き)

No.	R ¹	R ²	R ³	R ⁴	(X) _l	(Y) _m	(Z) _n	物 性
106	H	H	H	H	2-Cl	4-CN	4-OCF ₃	nD 1.5892(10°C)
107	H	H	H	H	3-Cl	2-CN	4-OCF ₃	m. p. 148 °C
108	H	H	H	H	4-F-3-Cl	4-CN	4-OCF ₃	m. p. 187-189 °C
109	H	H	H	H	4-F-3-Cl	4-CN	4-Cl	m. p. 184 °C
110	H	H	H	H	3-SCH ₃	4-CN	4-OCF ₃	m. p. 126 °C
111	H	H	H	H	3-SCH ₃	4-CN	4-Br	m. p. 162.6-163.1 °C
112	H	H	H	H	3-SOCH ₃	4-CN	4-OCF ₃	m. p. 179.0-181.6 °C
113	H	H	H	H	3-SOCH ₃	4-CN	4-Br	m. p. 129.8-130.6 °C
114	H	H	H	H	3-SO ₂ CH ₃	4-CN	4-OCF ₃	m. p. 212-214 °C
115	H	H	H	H	3-SO ₂ CH ₃	4-CN	4-Br	m. p. 199.5-200.1 °C
116	H	H	H	H	3-Cl	4-C=CH	4-OCF ₃	m. p. 173.8 °C

【0009】第1表中、物性がペースト状物のNMRデータを示す。

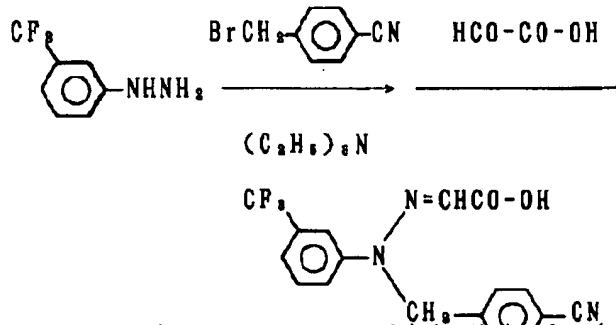
第 2 表

No.	NMR (CDCl ₃ /TMS, δ 値(ppm)]
70	1.82(3H, s), 4.72(2H, s), 6.73-7.80(12H, m), 8.95(1H, s).

以下に本発明の代表的な実施例を示すが本発明はこれらに限定されるものではない。

【0010】実施例 1

1-1. 2-[N-(4-シアノベンジル)-N-(3-トリフルオロメチルフェニル)]ヒドラゾノ酢酸の製造

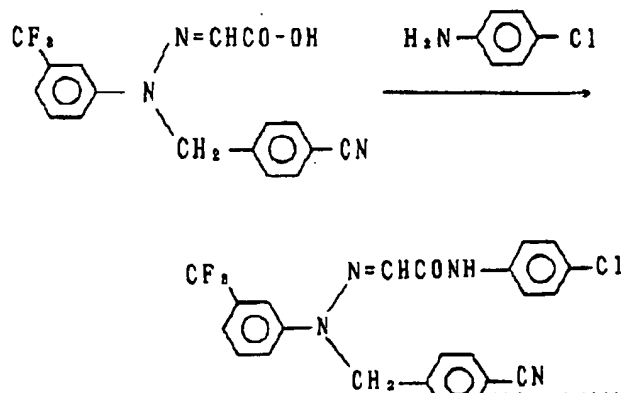


3-トリフルオロメチルフェニルヒドラジン 13.46 g (76.5ミリモル) をトルエン 100ml に溶解し、トリエチルアミン 8.12 g (80.4ミリモル) 及び 4-シアノベンジルブロミド 14.99 g (76.5ミリモル) を加え、3時間加熱下に反応を行った。反応終了後、反応液を水洗 (50ml×2) し有機層を濃縮し、次いで濃縮物をエタノール 80ml に溶解し、氷冷下に 40% グリオキシル酸水溶液 11.51 g (62.2ミリモル) を滴下し、室温下に 2時間攪拌を行った。反応終了後、目的物を含む反応溶液から溶媒を留去し、水 50

ml を加え、酢酸エチル (100ml×2) で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮して析出した結晶をヘキサノール-エーテル混合液で洗浄し、13.02 g の目的物を得た。

物性: m.p. 220℃ 収率 60.2%

【0011】1-2. 2-[N-(4-シアノベンジル)-N-(3-トリフルオロメチルフェニル)]ヒドラゾノ 4-クロロアセトアニリドの製造 (化合物 No. 39)



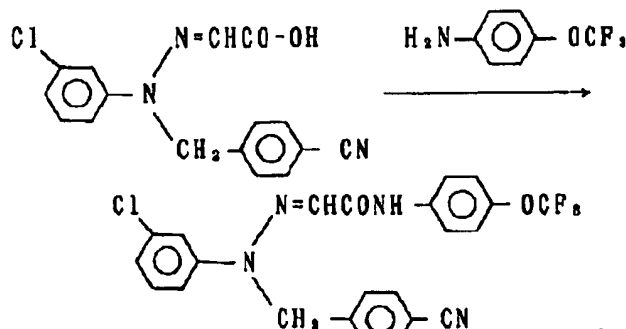
1-1 で得られた 2-[N-(4-シアノベンジル)-N-(3-トリフルオロメチルフェニル)]ヒドラゾノ酢酸 0.59 g (1.7ミリモル) を四塩化炭素 7ml に懸濁し、塩化チオニル 0.40 g (3.4ミリモル) を加え、1.5時間加熱還流した。反応終了後、反応溶媒を減圧下に留去して得られた酸クロリドを、4-クロロアニリン 0.62 g (1.7ミリモル) 及びトリエチルアミン 0.37 g (3.7ミリモル) をテトラヒドロフ

ラン 10ml に溶解した溶液に加え、室温下で 1時間攪拌を行った。反応終了後、反応液に水 10ml を加えて目的物を酢酸エチル (100ml×2) で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮した。得られた残渣をシリカゲルカラムクロマトグラフィー (ヘキサノール-酢酸エチル) で精製し、0.51 g の目的物を得た。

物性 m.p. 164-165℃ 収率 65.0%.

【0012】実施例2 2-[N-(3-クロロフェニル)-N-(4-シアノベンジル)]ヒドラゾノ 4-

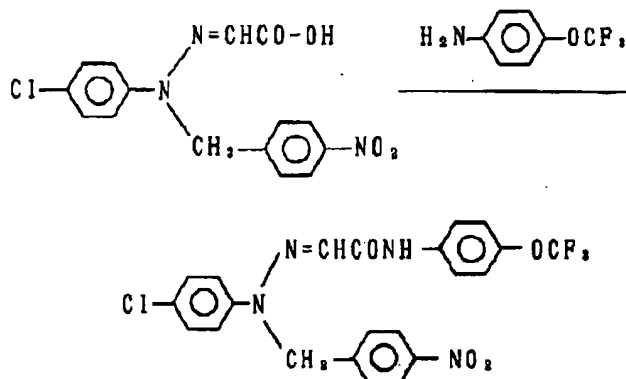
トリフルオロメトキシアセトアニリドの製造 (化合物No. 22)



1-1と同様にして製造した2-[N-(3-クロロフェニル)-N-(4-シアノベンジル)]ヒドラゾノ酢酸1.50g(4.8ミリモル)、ヨウ化2-クロロ-1-メチルピリジニウム1.34g(5.3ミリモル)、4-トリフルオロメトキシアニリン0.85g(4.8ミリモル)をピリジン20mlに溶解し3時間加熱還流した。反応終了後、溶媒を留去し、水30mlを加えて目的物を酢酸エチル(50ml×2)で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮した。

得られた残渣をシリカゲルカラムクロマトグラフィー(ヘキサン-酢酸エチル)で精製して1.64gの目的物を得た。
物性 m.p. 160.5-162.0℃ 収率 72.3%.

【0013】実施例3 2-[N-(4-クロロフェニル)-N-(4-ニトロベンジル)]ヒドラゾノ 4-トリフルオロメトキシアセトアニリドの製造 (化合物No. 28)

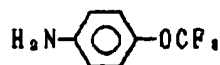
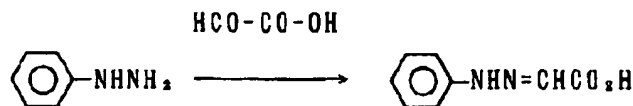


1-1と同様にして製造した2-[N-(4-クロロフェニル)-N-(4-ニトロベンジル)]ヒドラゾノ酢酸1.30g(3.9ミリモル)及びカルボニルジイミダゾール0.63g(3.9ミリモル)をテトラヒドロフラン10mlに溶解し、室温下に5時間攪拌を行った。反応終了後、水30mlを加えて酢酸エチル(50ml×2)で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮して得られた残渣をピリジン20mlに溶解し、4-トリフルオロメトキシアニリン0.69g(3.9ミリモル)及び4-ジメチルアミノピリジン0.10g(0.8ミリモル)を加えて12時間加熱還

流下に攪拌を行った。反応終了後、溶媒を留去して水30mlを加え、目的物を酢酸エチル(50ml×2)で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮して得られた残渣をシリカゲルカラムクロマトグラフィー(ヘキサン-酢酸エチル)で精製し0.95gの目的物を得た。
物性 m.p. 111.0-115.1℃ 収率 49.5%.

【0014】実施例4

4-1. 2-フェニルヒドラゾノ 4-トリフルオロメトキシアセトアニリドの製造

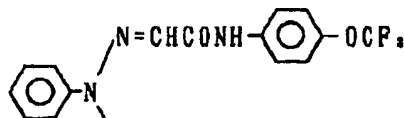
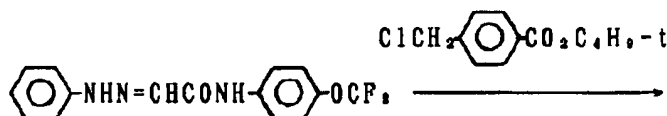


フェニルヒドラジン 30.24 g (0.28 モル) をエタノール 200 ml に溶解し、氷冷下に 40% グリオキシル酸水溶液 51.80 g (0.28 モル) を滴下し、室温下に 2 時間攪拌した。反応終了後、溶媒を減圧下に留去して析出した結晶をヘキサン-エーテル混合液で洗浄することにより、フェニルヒドラゾノ酢酸 20.2 g を得た (収率 43.9%)。得られたフェニルヒドラゾノ酢酸 7.81 g (47.6 ミリモル) 及びトリエチルアミン 10.58 g (104.7 ミリモル) をジクロロメタン 30 ml に溶解した溶液を、ヨウ化 2-クロロ-1-メチルピリジニウム 12.17 g (47.6 ミリモル) 及び 4-トリフルオロメトキシアニリン 8.43 g (47.6 ミリモル) をジクロロメタン 100 ml に溶解

した溶液に滴下し、室温下に 5 時間攪拌を行った。反応終了後、溶媒を留去して水 50 ml を加え、目的物を酢酸エチル (100 ml × 2) で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮し、得られた残渣をシリカゲルカラムクロマトグラフィー (ヘキサン-酢酸エチル) で精製して 7.62 g の目的物を得た。

物性 m.p. 151.2-154.3℃ 収率 49.6%.

【0015】4-2. tert-ブチル 4-[2-(4-トリフルオロメトキシフェニルカルバモイルメチル-N-フェニルヒドラゾノ-N-メチル)安息香酸の製造 (化合物 No. 11)



4-1 で得られたフェニルヒドラゾノ 4-トリフルオロメトキシアセトアニリド 0.71 g (2.2 ミリモル) をジメチルホルムアミド 20 ml に溶解し、氷冷下にカリウム tert-ブトキシド 0.27 g (2.4 ミリモル) 及び tert-ブチル 4-クロロメチル安息香酸 0.54 g を加え、室温下に 3 時間反応を行った。反応終了後、氷水 50 ml を加えて目的物を酢酸エチル (100 ml × 2) で抽出し、抽出液を無水硫酸ナトリウムで乾燥し、減圧下に濃縮して得られた残渣をシリカゲルカラムクロマトグラフィー (ヘキサン-酢酸エチル) で精製し、0.70 g の目的物を得た。

物性 m.p. 142.2-143.7℃ 収率 70.0%.

【0016】本発明の一般式(I)で表されるヒドラゾノ誘導体を有効成分とする農園芸用殺虫剤は、水稻、野菜、果樹、その他の作物及び花卉等を加害する各種農林、園芸、貯穀害虫や衛生害虫或いは線虫等の害虫防除に適用しており、例えばリンゴコカクモンハマキ (adoxophyes orana fasciata)、チャノコカクモンハマキ (Adoxo-

phys sp.)、リンゴシンクイ (Grapholita inopinata)、ナシヒメシンクイガ (Grapholita mlesla)、マメシンクイガ (Leguminivora glycinivorella)、クワハマキ (Olethreutes mori)、チャノホソガ (Caloptilia theviora)、リンゴホソガ (Caloptilia zachrysa)、キンモンホソガ (Phyllonorycterringtoniella)、ナシホソガ (Spulerina astauraota)、モンシロチョウ (Pieris rapae crucivora)、オオタバコガ類 (Heliothis sp.)、コドリナガ (L-aspeyresia pomonella)、コナガ (Plutella xylostella)、リンゴヒメシンクイ (Argyresthia conjugella)、モモシンクイガ (Carposina niponensis)、ニカメイガ (Chilo suppressalis)、コブノメイガ (Cnaphalocrocis medinalis)、チャマダラメイガ (Ephestia elutella)、クワノメイガ (Glyphodes pyloalis)、サンカメイガ (Scirpophaga incertulas)、イチモンジセセリ (Parnara guttata)、アワヨトウ (Pseudaletia separata)、イネヨトウ (Sesamia inferens)、ハスモンヨトウ (Spodoptera litura)、シロイチモンジヨトウ (Spodopte

ra exigua)等の鱗翅目害虫、フタテンヨコバイ (Macrostoteles fasci-frons)、ツマグロヨコバイ (Nephotetix cincticeps)、トビイロウンカ (Nilaparvata lugens)、セジロウンカ (Sogatella furcifera)、ミカンキジラミ (Diaphorina citri)、ブドウコナジラミ (Aleurolobus taenabae)、タバココナジラミ (Bemisia tabaci)、オンシツコナジラミ (Trialeurodes vaporariorum)、ニセダイコンアブラムシ (Lipaphis erysimi)、モモアカアブラムシ (Myzus persicae)、ツノロウムシ (Ceroplastes ceriferus)、ミカンワタカイガラムシ (Pulvinaria aurantii)、ミカンマルカイガラムシ (Pseudonidiaduplex)、ナシマルカイガラムシ (Comstockaspis perniciosus)、ヤノネカイガラムシ (Unaspis yanonensis)等の半翅目害虫、ネグサレセンチュウ (Pratylenchus sp.)、ヒメコガネ (Anomala rufocuprea)、マメコガネ (Popillia japonica)、タバコシバンムシ (Lasioderma serricorne)、ヒラタキクイムシ (Lyctus brunneus)、ニジウヤホシテントウ (Epilachna vigintioctopunctata)、アズキノウムシ (Callosobruchus chinensis)、ヤサイノウムシ (Lisstroderes costirostris)、コクゾウムシ (Sitophilus zeamais)、ワタミゾウムシ (Anthonomus grandis grandis)、イネミズゾウムシ (Lissorhoptrus oryzophilus)、ウリハムシ (Aulacophora femoralis)、イネドロオイムシ (Oulema oryzae)、キスジノミハムシ (Phyllotreta striolata)、コクゾウムシ (Sitophilus zeamais)、マツノキクイムシ (Tomocis piniperda)、コロラドポテトビートル (Leptinotarsa decemlineata)、メキシカンビーンビートル (Epilachna varivestis)、コーンルートワーム類 (Diabrotica sp.)、等の甲虫目害虫、ウリミバエ (Dacus (Zeugodacus) cucurbitae)、ミカンコミバエ (Dacus (Bactrocera) dorsalis)、イネハモグリバエ (Agromyza oryzae)、タマネギバエ (Delia antiqua)、タネバエ (Delia platura)、ダイズサヤタマバエ (Asphondylia sp.)、イエバエ (Musca domestica)、アカイエカ (Culex pipiens pipiens)等の双翅目害虫、ミナミネグサレセンチュウ (Pratylenchus coffeae)、ジャガイモシストセンチュウ (Globodera rostochiensis)、ネコブセンチュウ (Meloidogyne sp.)、ミカンネセンチュウ (Tylenchulus semipenetrans)、ニセネグサレセンチュウ (Aphelenchus avenae)、ハガレセンチュウ (Aphelenchoides ritzemabosi)等のハリセンチュウ目害虫等に対しても殺虫効果を有し、特に鱗翅目、甲虫目等の害虫に対しては顕著な効果を有するものである。尚、学名等は農林有害動物・昆虫名鑑1987年版(日本応用動物昆虫学会編)による。

【0017】本発明の農園芸用殺虫剤は水田、果樹、野菜、その他の作物及び花卉等を加害する前記害虫あるいは衛生害虫に対して顕著な殺虫効果を有するものである

ので、害虫類の発生が予測される時期に合わせて、害虫類の発生前又は発生が確認された時点で水田、果樹、野菜、その他の作物、花卉等の水田水、茎葉又は土壌等及び衛生害虫にあっては人畜に加害する上記害虫の発生若しくは発生が予測される家屋内、家屋周辺の溝等に処理することにより本発明の殺虫剤の所期の効果が奏せられるものである。しかし、本発明はこれらの態様のみに限定されるものではない。本発明の一般式(I)で表されるヒドラゾン誘導体を農園芸用殺虫剤として使用する場合、農薬製剤上の常法に従い、使用上都合の良い形状に製剤して使用するのが一般的である。即ち、本発明の一般式(I)で表されるヒドラゾン誘導体は、これらを適当な不活性担体に、又は必要に応じて補助剤と一緒に、適当な割合に配合して溶解、分離、懸濁、混合、含浸、吸着若しくは付着させ、適宜の剤形、例えば懸濁剤、乳剤、液剤、水和剤、粒剤、粉剤、錠剤等に製剤して使用すれば良い。本発明で使用できる不活性担体としては固体又は液体の何れであっても良く、固体の担体になりうる材料としては、例えばダイズ粉、穀物粉、木粉、樹皮粉、鯉粉、タバコ茎粉、クルミ殻粉、ふすま、繊維素粉末、植物エキスを抽出後の残渣、粉碎合成樹脂等の合成重合体、粘土類(例えばカオリン、ベントナイト、酸性白土等)、タルク類(例えばタルク、ピロフィライト等)、シリカ類(例えば珪藻土、珪砂、雲母、ホワイカーボン〔含水微粉珪素、含水珪酸ともいわれる合成高分散珪酸で、製品により珪酸カルシウムを主成分として含むものもある。〕)、活性炭、イオウ粉末、軽石、焼成珪藻土、レンガ粉碎物、フライアッシュ、砂、炭酸カルシウム、磷酸カルシウム等の無機鉱物性粉末、硫酸、燐安、硝安、尿素、塩安等の化学肥料、堆肥等を挙げることができ、これらは単独で若しくは二種以上の混合物の形で使用される。

【0018】液体の担体になりうる材料としては、それ自体溶媒能を有するものの他、溶媒能を有さずとも補助剤の助けにより有効成分化合物を分散させることとなるものから選択され、例えば代表例として次に挙げる担体を例示できるが、これらは単独で若しくは二種以上の混合物の形で使用され、例えば水、アルコール類(例えばメタノール、エタノール、イソプロパノール、ブタノール、エチレングリコール等)、ケトン類(例えばアセトン、メチルエチルケトン、メチルイソブチルケトン、ジイソブチルケトン、シクロヘキサノン等)、エーテル類(例えばエチルエーテル、ジオキサン、セロソルブ、ジプロピルエーテル、テトラヒドロフラン等)、脂肪族炭化水素類(例えばケロシン、鉱油等)、芳香族炭化水素類(例えばベンゼン、トルエン、キシレン、ソルベントナフサ、アルキルナフタレン等)、ハロゲン化炭化水素類(例えばジクロロエタン、クロロホルム、四塩化炭素、塩素化ベンゼン等)、エステル類(例えば酢酸エチル、ジイソブチルフタレート、ジブチルフタレート、ジ

オクルフタレート等)、アミド類(例えばジメチルホルムアミド、ジエチルホルムアミド、ジメチルアセトアミド等)、ニトリル類(例えばアセトニトリル等)、ジメチルスルホキシド類等を挙げることができる。他の補助剤としては次に例示する代表的な補助剤をあげることができ、これらの補助剤は目的に応じて使用され、単独で、ある場合は二種以上の補助剤を併用し、又ある場合には全く補助剤を使用しないことも可能である。

【0019】有効成分化合物の乳化、分散、可溶化及び/又は湿潤の目的のために界面活性剤が使用され、例えばポリオキシエチレンアルキルエーテル、ポリオキシエチレンアルキルアリールエーテル、ポリオキシエチレン高級脂肪酸エステル、ポリオキシエチレン樹脂酸エステル、ポリオキシエチレンソルビタンモノラウレート、ポリオキシエチレンソルビタンモノオレエート、アルキルアリールスルホン酸塩、ナフタレンスルホン酸縮合物、リグニンスルホン酸塩、高級アルコール硫酸エステル等の界面活性剤を例示することができる。又、有効成分化合物の分散安定化、粘着及び/又は結合の目的のために、次に例示する補助剤を使用することもでき、例えばカゼイン、ゼラチン、澱粉、メチルセルロース、カルボキシメチルセルロース、アラビアゴム、ポリビニルアルコール、松根油、糠油、ペントナイト、リグニンスルホン酸塩等の補助剤を使用することもできる。固体製品の流動性改良のために次に挙げる補助剤を使用することもでき、例えばワックス、ステアリン酸塩、磷酸アルキルエステル等の補助剤を使用できる。懸濁性製品の解こう

剤として、例えばナフタレンスルホン酸縮合物、縮合磷酸塩等の補助剤を使用することもできる。消泡剤としては、例えばシリコーン油等の補助剤を使用することもできる。

【0020】有効成分化合物の配合割合は必要に応じて加減することができ、例えば粉剤或いは粒剤とする場合は0.01~50重量%、又乳剤或いは水和剤とする場合も同様0.01~50重量%が適当である。本発明の一般式(I)で表されるヒドラゾン誘導体を有効成分とする農園芸用殺虫剤は、各種害虫を防除するために、そのまま、又は水等で適宜希釈し、若しくは懸濁させた形で害虫防除に有効な量を当該害虫に、又は当該害虫の発生若しくは成育が好ましくない場所に適用して使用すればよい。本発明の一般式(I)で表されるヒドラゾン誘導体を有効成分とする農園芸用殺虫剤の使用量は種々の因子、例えば目的、対象害虫、作物の生育状況、害虫の発生傾向、天候、環境条件、剤型、施用方法、施用場所、施用時期等により変動するが、有効成分化合物として10アール当たり0.1g~5Kgの範囲から目的に応じて適宜選択すれば良い。本発明の一般式(I)で表されるヒドラゾン誘導体を有効成分とする農園芸用殺虫剤を更に防除対象害虫、防除適期の拡大のため、或いは薬量の低減をはかる目的で他の殺虫剤又は殺菌剤と混合して使用することも可能である。以下に本発明の代表的な処方例及び試験例を示すが、本発明はこれらに限定されるものではない。尚、処方例中、部とあるのは重量部を示す。

【0021】処方例1

本発明化合物	50部
キシレン	40部
ポリオキシエチレンノニルフェニルエーテルと	
アルキルベンゼンスルホン酸カルシウムとの混合物	10部

以上を均一に混合溶解して乳剤とする。

処方例2

本発明化合物	3部
クレー粉末	82部
珪藻土粉末	15部

以上を均一に混合粉碎して粉剤とする。

処方例3

本発明化合物	5部
ペントナイトとクレーの混合粉末	90部
リグニンスルホン酸カルシウム	5部

以上を均一に混合し、適量の水を加えて混練し、造粒、乾燥して粒剤とする。

処方例4

本発明化合物	20部
カオリンと合成高分散珪酸	75部
ポリオキシエチレンノニルフェニルエーテルとアル	
キルベンゼンスルホン酸カルシウムとの混合物	5部

以上を均一に混合粉碎して水和剤とする。

【0022】試験例1 ハスモンヨトウ (*Spodoptera litura*) に対する殺虫試験
本発明化合物を有効成分とする薬剤を500ppmに希釈した薬液にキャベツ葉片(品種:四季穫)を約30秒間

浸漬した。風乾後に直径9cmのプラスチックシャーレに入れ、ハスモンヨトウ2令幼虫を接種した後、蓋をして25℃恒温室に静置した。接種8日後に生虫数を調査し、下記の式により死虫率を算出し、下記の基準に従って判定を行った。

$$\text{補正死虫率 (\%)} = \frac{\text{死虫数}}{\text{接種虫数}} \times 100$$

判定基準.

A・・・死虫率100%

B・・・死虫率99%~90%

C・・・死虫率89%~80%

D・・・死虫率79%~50%

結果を第3表に示す。

【0023】

第 3 表

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
3	500	C	31	500	A
4	500	A	32	500	A
5	500	A	33	500	A
7	500	D	34	500	A
8	500	D	38	500	A
9	500	A	40	500	A
10	500	A	41	500	A
11	500	C	47	500	A
14	500	A	53	500	A
17	500	A	54	500	A
18	500	A	64	500	D
19	500	A	65	500	C
20	500	A	73	500	A
21	500	A	76	500	A
22	500	A	77	500	A
23	500	D	78	500	A
25	500	A	79	500	A
26	500	A	80	500	A
27	500	C	81	500	A
28	500	A	83	500	C
29	500	A	84	500	A
30	500	A	87	500	A

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
88	500	D	104	500	A
89	500	D	108	500	A
91	500	C	110	500	A
94	500	D	111	500	D
95	500	D	112	500	A
100	500	A	113	500	D
102	500	D	115	500	D
103	500	A	116	500	A

【0024】試験例2 コクゾウ (*Sitophilus zeamais*) 成虫に対する殺虫試験

本発明化合物を有効成分とする薬剤を200ppmに希釈した薬液に玄米を約30秒間浸漬した。風乾後に直径4cmのガラスシャーレに入れ、コクゾウ成虫を接種した後、蓋をして25℃恒温室に静置した。接種8日後に生

死虫数を調査し、試験例1に従って死虫率を算出し、試験例1の基準に従って判定を行った。1区10頭3連制。結果を第4表に示す。

【0024】

No.	濃度 (ppm)	判定	No.	濃度 (ppm)	判定
4	200	D	9	200	D
7	200	B	17	200	B
8	200	C	18	200	C

第4表(続き)

No.	濃度 (ppm)	判定	No.	濃度 (ppm)	判定
19	200	C	64	200	A
20	200	C	65	200	A
21	200	A	72	200	C
22	200	A	73	200	A
27	200	D	75	200	A
28	200	C	76	200	A
30	200	A	77	200	A
31	200	D	78	200	A
38	200	A	79	200	A
39	200	A	80	200	A
40	200	A	81	200	A
41	200	A	82	200	A
42	200	A	83	200	A
43	200	D	84	200	A
47	200	A	85	200	A
50	200	B	86	200	D
53	200	A	87	200	A
54	200	A	88	200	A
55	200	A	89	200	A
56	200	A	90	200	A
57	200	A	91	200	A
62	200	D	92	200	A
63	200	B	93	200	A

第 4 表 (続き)

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
94	200	A	106	200	A
95	200	A	107	200	A
96	200	A	108	200	A
97	200	D	109	200	A
98	200	A	110	200	A
100	200	A	111	200	A
101	200	A	112	200	A
102	200	A	113	200	A
103	200	A	114	200	A
104	200	A	115	200	A
105	200	A	116	200	A

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(72)Inventor : HINO TOMOKAZU

ANDOU NOBUHARU

HAMAGUCHI HIROSHI

KANEOKA ATSUSHI

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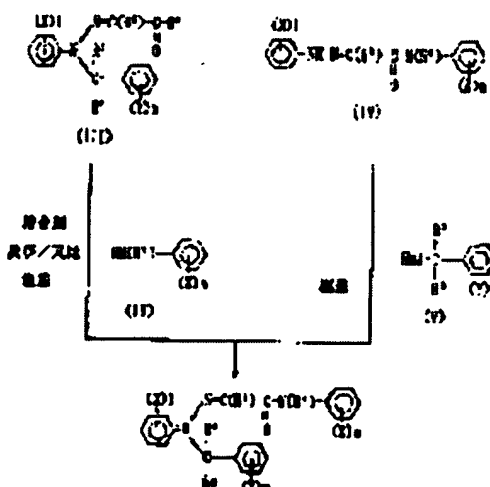
Priority number : 02312414 Priority date : 17.11.1990 Priority country : JP

(54) HYDRAZONE DERIVATIVE, ITS PRODUCTION, ITS USE AND METHOD FOR UTILIZING THE SAME DERIVATIVE

(57)Abstract:

PURPOSE: To obtain a new hydrazine derivative useful as an agricultural and horticultural insecticide having excellently insecticidal effects with a small amount, strong effects especially on lepidopterous insect pests and beetles.

CONSTITUTION: A compound of formula I (R1 to R4 are H or lower alkyl; X to Z are halogen, NO₂, lower alkyl, lower haloalkyl, lower alkoxy, lower alkylthio, lower alkylsulfinyl or lower alkylsulfonyl; further Y to Z are CN, lower haloalkoxy, lower haloalkylthio, lower



haloalkylsulfinyl, lower haloalkylsulfonyl, etc.; l to n are 0-5 integer) such as 2-[N-(4-cyanobenzyl)-N-(3-trifluoromethylphenyl)]hydrazono-4-chloroacetanilide. The compound is obtained by reacting a compound of formula II (R5 is halogen or OH) with a compound of formula III or a compound of formula IV with a compound of formula V (Hal is halogen).

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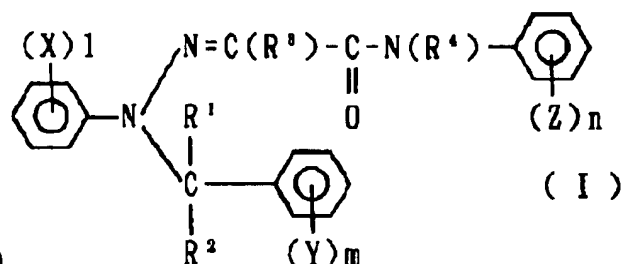
[Date of requesting appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]



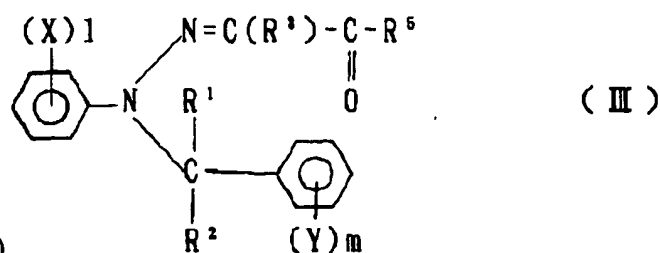
[Claim 1] General formula (I)

Or may differ and a hydrogen atom or a low-grade alkyl group is shown. the inside of a formula, and R1, R2, R3 and R4 -- ** -- the same -- X is the same -- or -- you may differ -- a halogen atom, a nitro group, and a low-grade alkyl group -- A low-grade halo alkyl group, lower alkoxy group, low-grade alkylthio group, and low-grade alkyl sulfinyl group or a low-grade alkyl sulfonyl group is shown. Y is the same -- or -- you may differ -- a halogen atom, a cyano group, and a nitro group -- A low-grade alkyl group and low-grade halo alkyl group, a lower alkoxy group, a low-grade haloalkoxy radical, A low-grade alkylthio group and low-grade alkyl sulfinyl group, a low-grade alkyl sulfonyl group, A low-grade halo alkylthio group, a low-grade halo alkyl sulfinyl group, a low-grade halo alkyl sulfonyl group, Or you may differ. a low-grade alkynyl group or a low-grade alkoxy carbonyl group is shown, and Z is the same -- A halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, A lower alkoxy group, low-grade haloalkoxy radical, low-grade alkylthio group, and low-grade halo alkylthio group, a low-grade alkyl sulfinyl group, a low-grade halo alkyl sulfinyl group, a low-grade alkyl sulfonyl group, a low-grade halo alkyl sulfonyl group, a low-grade halo alkylsulfonyloxy radical, a low-grade alkyl carbonyl group, or a phenoxy group is shown, and l, m, and n show the integer of each 0-5. The hydrazone derivative expressed.

[Claim 2] general formula (I) Or you may differ. it sets and R1, R2, R3, and R4 are the same -- Or you may differ. a hydrogen atom or a low-grade alkyl group is shown, and X is the same -- Or you may differ. a halogen atom, a low-grade alkyl group, or a low-grade halo alkyl group is shown, and Y is the same -- A cyano group, nitro group, low-grade alkyl group, and low-grade halo alkyl group, a low-grade halo alkylthio group, or a low-grade halo alkyl sulfinyl group is shown. Z is the same or the hydrazone derivative given in the 1st term of a claim in which you may differ and a halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, a lower alkoxy group, or a low-grade haloalkoxy radical is shown and which l, m, and n show the integer of 0-3 respectively.

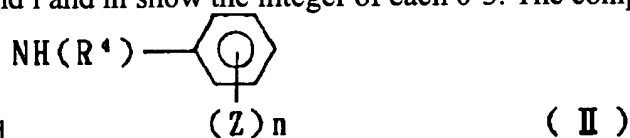
[Claim 3] general formula (I) Or you may differ. it sets and R1, R2, R3, and R4 are the same -- Or you may differ. a hydrogen atom or a low-grade alkyl group is shown, and X is the same -- Or you may differ. a halogen atom, a low-grade alkyl group, or a low-grade halo alkyl group is shown, and Y is the same -- A cyano group, a nitro group, or a low-grade halo alkyl sulfinyl group is shown, and Z is the same or the hydrazone derivative given in the 2nd term of a claim in which you may differ and a halogen atom, a low-grade halo alkyl group, or a low-grade haloalkoxy radical is shown and which l, m, and n show the integer of 1-3 respectively.

[Claim 4] General formula (I) Hydrazone derivative given in the 3rd term of a claim which was set, X of a piece permuted by the 3rd place at least, Y of a piece permuted by the 4th place at least, and Z of a piece permuted by the 4th place at least.



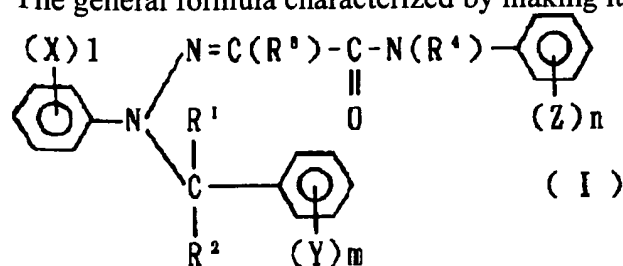
[Claim 5] General formula (III)

Or may differ and a hydrogen atom or a low-grade alkyl group is shown. the inside of a formula, and R1, R2 and R3 are the same -- Or you may differ. R5 shows a halogen atom or a hydroxyl group -- X is the same -- A halogen atom, nitro group, low-grade alkyl group, and low-grade halo alkyl group, a lower alkoxy group, A low-grade alkylthio group and low-grade alkyl sulfinyl group or a low-grade alkyl sulfonyl group is shown. Y is the same -- or -- you may differ -- a halogen atom, a cyano group, and a nitro group -- A low-grade alkyl group and low-grade halo alkyl group, a lower alkoxy group, a low-grade haloalkoxy radical, A low-grade alkylthio group and low-grade alkyl sulfinyl group, a low-grade alkyl sulfonyl group, a low-grade halo alkylthio group, a low-grade halo alkyl sulfinyl group, a low-grade halo alkyl sulfonyl group, a low-grade alkynyl group, or a low-grade alkoxy carbonyl group is shown, and l and m show the integer of each 0-5. The compound and general formula (II) which are

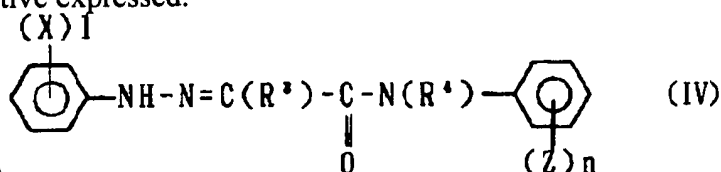


expressed

Or you may differ. R4 shows a hydrogen atom or a low-grade alkyl group among a formula, and Z is the same -- A halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, A lower alkoxy group, low-grade haloalkoxy radical, low-grade alkylthio group, and low-grade halo alkylthio group, a low-grade alkyl sulfinyl group, a low-grade halo alkyl sulfinyl group, a low-grade alkyl sulfonyl group, a low-grade halo alkyl sulfonyl group, a low-grade halo alkylsulfonyloxy radical, a low-grade alkyl carbonyl group, or a phenoxy group is shown, and n shows the integer of 0-5. The general formula characterized by making it react with the aniline expressed (I)



(-- R1, R2, R3, R4, X, Y, Z, l, m, and n are the same as the above among a formula.) -- the manufacture approach of a hydrazone derivative expressed.



[Claim 6] General formula (IV)

Or you may differ. the inside of a formula, and R3 and R4 are the same -- or you may differ and a hydrogen atom or a low-grade alkyl group is shown -- X is the same -- A halogen atom, nitro group, low-grade alkyl group, and low-grade halo alkyl group, a lower alkoxy group, A low-grade alkylthio group and low-grade alkyl sulfinyl group or a low-grade alkyl sulfonyl group is shown. Z is the same -- or -- you may differ -- a halogen atom, a nitro group, and a cyano group -- A low-grade alkyl group and

$$\text{Hal}-\text{C} \begin{array}{l} \text{R}^1 \\ | \\ \text{R}^2 \end{array} - \text{C}_6\text{H}_4 - (\text{Y})_m$$
$$\begin{array}{c}
 \text{(X)}_1 \\
 | \\
 \text{C}_6\text{H}_4 - \text{N} \begin{cases} \nearrow \text{N}=\text{C}(\text{R}^3) - \text{C}(=\text{O}) - \text{N}(\text{R}^4) - \text{C}_6\text{H}_4(\text{Z})_n \\ \searrow \text{R}^1 \\ | \\ \text{C} - \text{C}_6\text{H}_4(\text{Y})_m \\ | \\ \text{R}^2 \end{cases}
 \end{array}
 \quad (\text{I})$$
$$\begin{array}{c}
 \text{(X)}_1 \\
 | \\
 \text{C}_6\text{H}_5 - \text{N} \begin{cases} \nearrow \text{N}=\text{C}(\text{R}^3) - \text{C}(=\text{O}) - \text{N}(\text{R}^4) - \text{C}_6\text{H}_4(\text{Z})_n \\ \searrow \text{R}^1 \\ | \\ \text{C} - \text{C}_6\text{H}_4(\text{Y})_m \\ | \\ \text{R}^2 \end{cases}
 \end{array}
 \quad (\text{I})$$

Or may differ and a hydrogen atom or a low-grade alkyl group is shown. the inside of a formula, and R1, R2, R3 and R4 -- ** -- the same -- X is the same -- or -- you may differ -- a halogen atom, a nitro group, and a low-grade alkyl group -- A low-grade halo alkyl group, lower alkoxy group, low-grade alkylthio group, and low-grade alkyl sulfinyl group or a low-grade alkyl sulfonyl group is shown. Y is the same -- or -- you may differ -- a halogen atom, a cyano group, and a nitro group -- A low-grade alkyl group and low-grade halo alkyl group, a lower alkoxy group, a low-grade haloalkoxy radical, A low-grade alkylthio group and low-grade alkyl sulfinyl group, a low-grade alkyl sulfonyl group, A low-grade halo alkylthio group, a low-grade halo alkyl sulfinyl group, a low-grade halo alkyl sulfonyl group, Or you may differ. a low-grade alkynyl group or a low-grade alkoxy carbonyl group is shown, and Z is the same -- A halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, A lower alkoxy group, low-grade haloalkoxy radical, low-grade alkylthio group, and low-grade halo alkylthio group, a low-grade alkyl sulfinyl group, a low-grade halo alkyl sulfinyl group, a low-grade alkyl sulfonyl group, a low-grade halo alkyl sulfonyl group, a low-grade halo alkylsulfonyloxy

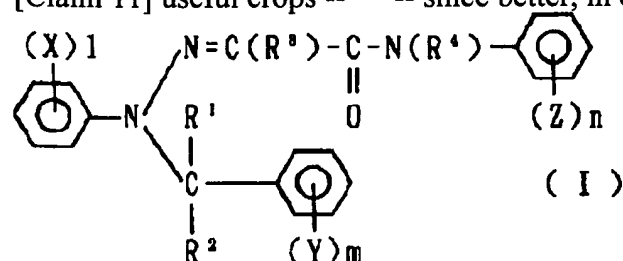
radical, a low-grade alkyl carbonyl group, or a phenoxy group is shown, and l, m, and n show the integer of each 0-5. The insecticide for plantation arts characterized by containing the hydrazone derivative expressed as an active principle.

[Claim 8] general formula (I) Or you may differ. it sets and R1, R2, R3, and R4 are the same -- Or you may differ. a hydrogen atom or a low-grade alkyl group is shown, and X is the same -- Or you may differ. a halogen atom, a low-grade alkyl group, or a low-grade halo alkyl group is shown, and Y is the same -- A cyano group, nitro group, low-grade alkyl group, and low-grade halo alkyl group, a low-grade halo alkylthio group, or a low-grade halo alkyl sulfinyl group is shown. Z is the same or the insecticide for plantation arts given in the 7th term of a claim in which you may differ and a halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, a lower alkoxy group, or a low-grade haloalkoxy radical is shown and which l, m, and n show the integer of 0-3 respectively.

[Claim 9] general formula (I) Or you may differ. it sets and R1, R2, R3, and R4 are the same -- Or you may differ. a hydrogen atom or a low-grade alkyl group is shown, and X is the same -- Or you may differ. a halogen atom, a low-grade alkyl group, or a low-grade halo alkyl group is shown, and Y is the same -- A cyano group, a nitro group, or a low-grade halo alkyl sulfinyl group is shown, and Z is the same or the insecticide for plantation arts given in the 8th term of a claim in which you may differ and a halogen atom, a low-grade halo alkyl group, or a low-grade haloalkoxy radical is shown and which l, m, and n show the integer of 1-3 respectively.

[Claim 10] General formula (I) Insecticide for plantation arts given in the 9th term of a claim which was set, X of a piece permuted by the 3rd place at least, Y of a piece permuted by the 4th place at least, and Z of a piece has permuted by the 4th place at least.

[Claim 11] useful crops -- ** -- since better, in order to prevent from ***** -- a general formula (I)



Or may differ and a hydrogen atom or a low-grade alkyl group is shown. the inside of a formula, and R1, R2, R3 and R4 -- ** -- the same -- X is the same -- or -- you may differ -- a halogen atom, a nitro group, and a low-grade alkyl group -- A low-grade halo alkyl group, lower alkoxy group, low-grade alkylthio group, and low-grade alkyl sulfinyl group or a low-grade alkyl sulfonyl group is shown. Y is the same -- or -- you may differ -- a halogen atom, a cyano group, and a nitro group -- A low-grade alkyl group and low-grade halo alkyl group, a lower alkoxy group, a low-grade haloalkoxy radical, A low-grade alkylthio group and low-grade alkyl sulfinyl group, a low-grade alkyl sulfonyl group, A low-grade halo alkylthio group, a low-grade halo alkyl sulfinyl group, a low-grade halo alkyl sulfonyl group, Or you may differ. a low-grade alkynyl group or a low-grade alkoxy carbonyl group is shown, and Z is the same -- A halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, A lower alkoxy group, low-grade haloalkoxy radical, low-grade alkylthio group, and low-grade halo alkylthio group, a low-grade alkyl sulfinyl group, a low-grade halo alkyl sulfinyl group, a low-grade alkyl sulfonyl group, a low-grade halo alkyl sulfonyl group, a low-grade halo alkylsulfonyloxy radical, a low-grade alkyl carbonyl group, or a phenoxy group is shown, and l, m, and n show the integer of each 0-5. ** characterized by processing the insecticide for plantation arts which contains the hydrazone derivative expressed as an active principle with the dose of 1g per 10a. - 5kg as an active principle -- since better -- the prevention approach of *****.

[Claim 12] general formula (I) Or you may differ. it sets and R1, R2, R3, and R4 are the same -- Or you may differ. a hydrogen atom or a low-grade alkyl group is shown, and X is the same -- Or you may differ. a halogen atom, a low-grade alkyl group, or a low-grade halo alkyl group is shown, and Y is the

same -- A cyano group, nitro group, low-grade alkyl group, and low-grade halo alkyl group, a low-grade halo alkylthio group, or a low-grade halo alkyl sulfinyl group is shown. Z is the same or the prevention approach given in the 11th term of a claim that may differ, a halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, a lower alkoxy group, or a low-grade haloalkoxy radical is shown, and l, m, and n show the integer of 0-3 respectively.

[Claim 13] general formula (I) Or you may differ. it sets and R1, R2, R3, and R4 are the same -- Or you may differ. a hydrogen atom or a low-grade alkyl group is shown, and X is the same -- Or you may differ. a halogen atom, a low-grade alkyl group, or a low-grade halo alkyl group is shown, and Y is the same -- A cyano group, a nitro group, or a low-grade halo alkyl sulfinyl group is shown, and Z is the same or the prevention approach given in the 12th term of a claim that may differ, a halogen atom, a low-grade halo alkyl group, or a low-grade haloalkoxy radical is shown, and l, m, and n show the integer of 1-3 respectively.

[Claim 14] General formula (I) The prevention approach given in the 13th term of a claim which was set, X of a piece permuted by the 3rd place at least, Y of a piece permuted by the 4th place at least, and Z of a piece permuted by the 4th place at least.

[Claim 15] The prevention approach given in the 14th term of a claim that a noxious insect is a Lepidoptera noxious insect or a Coleoptera noxious insect.

[Translation done.]

* NOTICES *

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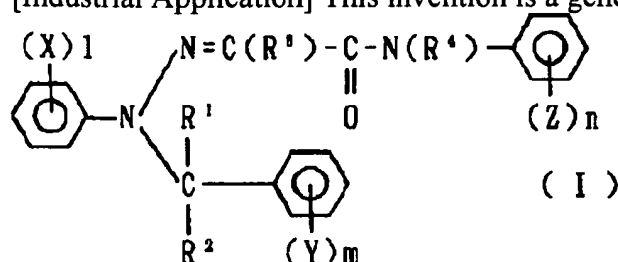
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is a general formula (I).



Or may differ and a hydrogen atom or a low-grade alkyl group is shown. the inside of a formula, and R1, R2, R3 and R4 -- ** -- the same -- X is the same -- or -- you may differ -- a halogen atom, a nitro group, and a low-grade alkyl group -- A low-grade halo alkyl group, lower alkoxy group, low-grade alkylthio group, and low-grade alkyl sulfinyl group or a low-grade alkyl sulfonyl group is shown. Y is the same -- or -- you may differ -- a halogen atom, a cyano group, and a nitro group -- A low-grade alkyl group and low-grade halo alkyl group, a lower alkoxy group, a low-grade haloalkoxy radical, A low-grade alkylthio group and low-grade alkyl sulfinyl group, a low-grade alkyl sulfonyl group, A low-grade halo alkylthio group, a low-grade halo alkyl sulfinyl group, a low-grade halo alkyl sulfonyl group, Or you may differ. a low-grade alkynyl group or a low-grade alkoxy carbonyl group is shown, and Z is the same -- A halogen atom, nitro group, cyano group, low-grade alkyl group, and low-grade halo alkyl group, A lower alkoxy group, low-grade haloalkoxy radical, low-grade alkylthio group, and low-grade halo alkylthio group, a low-grade alkyl sulfinyl group, a low-grade halo alkyl sulfinyl group, a low-grade alkyl sulfonyl group, a low-grade halo alkyl sulfonyl group, a low-grade halo alkylsulfonyloxy radical, a low-grade alkyl carbonyl group, or a phenoxy group is shown, and l, m, and n show the integer of each 0-5. It is related with the hydrazone derivative expressed, its manufacture approach, and the insecticide list for plantation arts at the operation.

[0002]

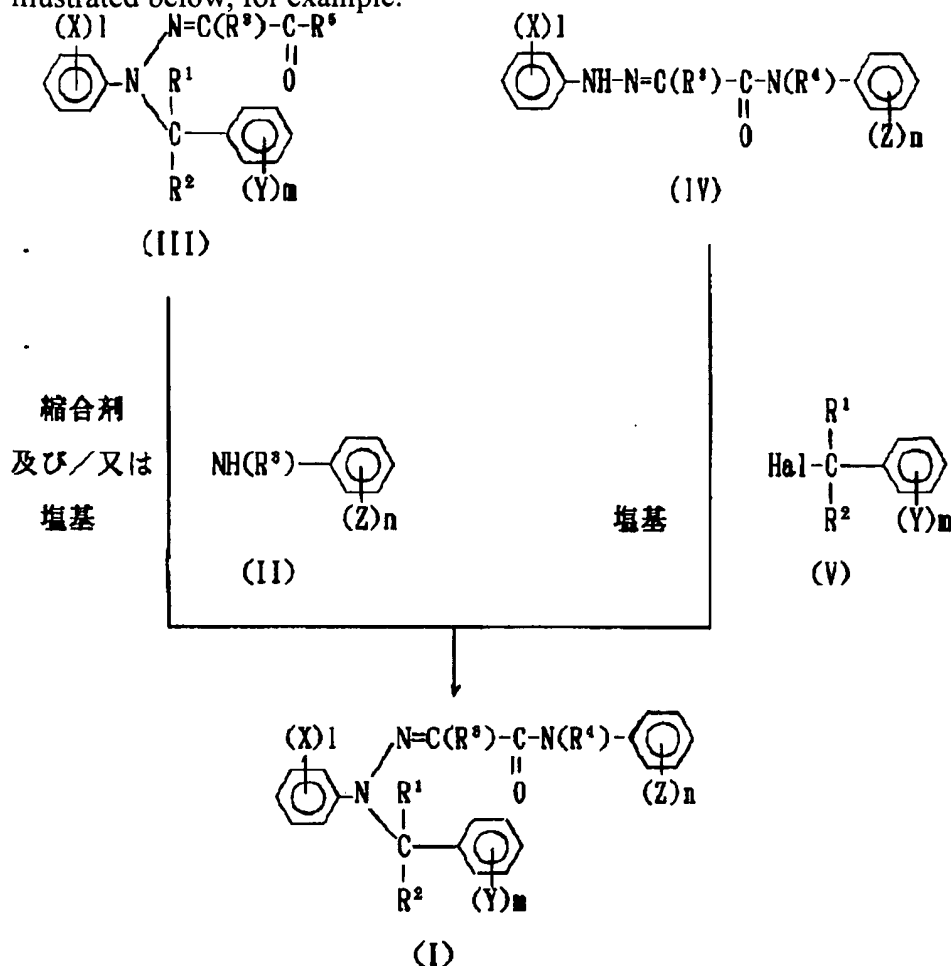
[Description of the Prior Art] Hydrazones are indicated by JP,48-91223,A, JP,54-122261,A, JP,56-45452,A, JP,63-93761,A, etc. as an insecticide and a pest control agent.

[Problem(s) to be Solved by the Invention] this invention person etc. is a general formula (I), as a result of repeating research wholeheartedly that a new insecticide should be created. Header this invention is completed for having the insect-killing effectiveness which neither publication nor suggestion is carried out to advanced-technology reference etc., but whose hydrazone derivative expressed is reference a non-indicated new molecular entity, and was excellent in the low dose.

[0003]

[Means for Solving the Problem] General formula of this invention (I) As the typical manufacture approach of a hydrazone derivative expressed, it can manufacture by the manufacture approach

illustrated below, for example.



(R₁, R₂, R₃, R₄, R₅, X, Y, Z, l, m, and n are the same as the above among a formula.)

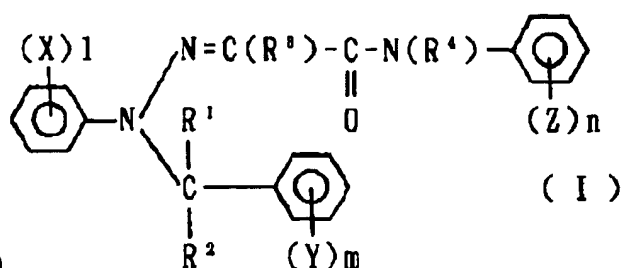
general formula (III) the aniline expressed with the compound expressed and a general formula (II) -- the bottom of existence of an inert solvent, and a base -- and -- or the compound and the general formula (V) which are made to react to the bottom of existence of a condensing agent or un-existing, or are expressed with a general formula (IV) making the halide expressed react to the bottom of existence of an inert solvent and a base -- general formula (I) The hydrazone derivative expressed can be manufactured. [0004] 1. General formula (III) -> As an inert solvent which can be used at a (general formula I) book reaction That what is necessary is just what does not check advance of this reaction remarkably For example, dichloromethane, Halogenated hydrocarbon, such as chloroform and a carbon tetrachloride, benzene, toluene, Nitril, such as aromatic hydrocarbon, such as a xylene, an acetonitrile, and a benzonitrile Chain-like ether, such as methyl cellosolve and diethylether, dioxane, Ketones, such as cyclic ether, such as a tetrahydrofuran, an acetone, and a methyl ethyl ketone Ester, such as ethyl acetate, N.N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), a pyridine, etc. can be illustrated, and these inert solvents may be used independently, and can also be mixed and used. An organic base or an inorganic base can be used as a base used at this reaction. As an inorganic base For example, a hydroxide or a carbonate of alkaline-earth-metal atoms, such as alkali-metal atoms, such as sodium and a potassium, calcium, and magnesium, etc., As the hydride of alkali-metal atoms, such as sodium hydride, and an organic base, triethylamine, A pyridine, N.N-dimethylaniline, 2, 6-lutidine, Being able to use 4-N and N-dimethylamino pyridine etc., the amount used is the amount of catalysts thru/or a general formula (III). It can be used to the compound expressed, choosing from the range of equimolar thru/or a superfluous mol.

[0005] As a condensing agent, KARUBOJI imidazo-RU, dicyclohexylcarbodiimide, iodation 2-chloro-

1-methyl pyridinium, etc. can be used, for example, and the amount used is a general formula (III). What is necessary is just to use it, choosing from the range of equimolar thru/or a superfluous mol to the compound expressed. Although what is necessary is just to carry out equimolar use of each reaction agent since this reaction is an equimolar reaction, aniline can also be used superfluously. Reaction temperature is [that what is necessary is just to choose from the range of a room temperature thru/or the boiling point region of the inert solvent to be used suitably] good to carry out to the bottom of heating preferably. What is necessary is just to choose from the range of several minutes thru/or 48 hours, although reaction time is not fixed with reacting weight, reaction temperature, etc. A conventional method, for example, solvent distilling off, solvent extraction, etc. can be performed from the reaction mixture containing the specified substance after reaction termination, and the specified substance can be manufactured by refining by the recrystallizing method, the column-chromatography method, etc. if needed.

[0006] 2. General formula (IV) -> The compound and general formula (V) which are expressed with a general formula (I) general formula (IV) It is a general formula (I) by making the halide expressed react to the bottom of existence of an inert solvent and a base. The hydrazone derivative expressed can be manufactured. That what is necessary is just what does not check advance of this reaction remarkably as an inert solvent which can be used at this reaction For example, alcohols, such as a methanol, ethanol, and propanol, dichloromethane, Halogenated hydrocarbon, such as chloroform and a carbon tetrachloride, benzene, toluene, Nitril, such as aromatic hydrocarbon, such as a xylene, an acetonitrile, and a benzonitrile Chain-like ether, such as methyl cellosolve and diethylether, dioxane, Ester, such as ketones, such as cyclic ether, such as a tetrahydrofuran, and an acetone, and ethyl acetate Dimethylformamide, dimethylacetamide, dimethyl sulfoxide, water, etc. can be illustrated, and these inert solvents may be used independently, and can also be mixed and used. An organic base or an inorganic base can be used as a base used at this reaction. As an inorganic base For example, a hydroxide or a carbonate of alkaline-earth-metal atoms, such as alkali-metal atoms, such as sodium and a potassium, calcium, and magnesium, etc., As the hydride of alkali-metal atoms, such as sodium hydride, and an organic base, a sodium METOKI side, Third class alkylamine [, such as an amination object of alkali-metal atoms, such as alcoholates of alkali-metal atoms, such as potassium t-butoxide, and a sodium amine, and triethylamine,], pyridine, 4-N, and N-dimethylamino pyridine etc. can be used.

[0007] What is necessary is just to use the amount of the base used, choosing it from the range of equimolar thru/or a superfluous mol to the compound expressed with a general formula (IV). This reaction is a general formula (V), although what is necessary is just to carry out equimolar use of each reaction agent since it is an equimolar reaction. The halide expressed can also be used superfluously. What is necessary is just to choose reaction temperature from the range of a room temperature thru/or the boiling point region of the inert solvent to be used suitably. What is necessary is just to choose from the range of several minutes thru/or 48 hours, although reaction time is not fixed with reacting weight, reaction temperature, etc. The specified substance can be manufactured after reaction termination by making it be the same as that of the aforementioned reaction. general formula (I) of this invention General formula (III) which is a raw material compound at the time of manufacturing the hydrazone derivative expressed the compound expressed -- Provisional Publication No. No. 223169 [62 to], a 64-70462 official report, J.Org.Chem., 417 (1941), Ber.56B, and 1060-1065 (1923) etc. -- it can manufacture by the approach of a publication. Moreover, compound expressed with a general formula (IV) It can manufacture by the approach of a publication to Collection Czech.Chem.Communs., 25, and 2651-2667 (1960). It is the general formula (I) of this invention below. Although illustrated to the 1st table, this invention is not limited to these compounds.



[0008] General formula (I)

(Following margin)

[Table 1]

第 1 表

No.	R ¹	R ²	R ³	R ⁴	(X) ₁	(Y) _m	(Z) _n	物 性
1	H	H	H	H	H	H	H	m. p. 172.1 °C
2	H	H	H	H	H	H	4-CH ₃	m. p. 155.2-152.8 °C
3	H	H	H	H	H	H	4-OCF ₃	m. p. 113.3-114.0 °C
4	H	H	H	H	H	4-Cl	4-CF ₃	m. p. 159.7 °C
5	H	H	H	H	H	4-Cl	4-OCF ₃	m. p. 137.8 °C
6	H	H	H	H	H	4-Cl	4-COCH ₃	m. p. 187.9 °C
7	H	H	H	H	H	4-CN	4-Cl	m. p. 163 °C
8	H	H	H	H	H	4-CN	4-CF ₃	m. p. 184-185 °C
9	H	H	H	H	H	4-CN	4-OCF ₃	m. p. 138 °C
10	H	H	H	H	H	4-CO ₂ CH ₃	4-OCF ₃	m. p. 159 °C
11	H	H	H	H	H	4-CO ₂ C ₆ H ₅ -t	4-OCF ₃	m. p. 142.2-143.7 °C
12	H	H	H	H	3-Cl	4-Cl	2-Cl	m. p. 135.5-137.0 °C
13	H	H	H	H	3-Cl	4-Cl	3-Cl	m. p. 136.3 °C
14	H	H	H	H	3-Cl	4-Cl	4-Cl	m. p. 143.5-144.0 °C
15	H	H	H	H	3-Cl	4-Cl	3-CH ₃	m. p. 128.5 °C
16	H	H	H	H	3-Cl	4-Cl	4-CH ₃	m. p. 149.6-150.0 °C
17	H	H	H	H	3-Cl	4-Cl	4-OCF ₃	m. p. 139.6-141.5 °C
18	H	H	H	H	3-Cl	4-NO ₂	4-Cl	m. p. 174.0-176.5 °C
19	H	H	H	H	3-Cl	4-NO ₂	4-OCF ₃	m. p. 151.6-151.7 °C
20	H	H	H	H	3-Cl	4-CN	4-Cl	m. p. 191.0-192.0 °C
21	H	H	H	H	3-Cl	4-CN	4-CF ₃	m. p. 202.9 °C


[Table 2]

第 1 表 (続 き)

No.	R ¹	R ²	R ³	R ⁴	(X) _l	(Y) _m	(Z) _n	物 性
22	H	H	H	H	3-Cl	4-CN	4-OCF ₃	m. p. 160.5-162.0 °C
23	H	H	H	H	3-Cl	4-CN	4-SCF ₃	m. p. 188.0 °C
24	H	H	H	H	3-Cl	4-CN	4-SOCF ₃	m. p. 206.1 °C
25	H	H	H	H	3-Cl	4-OCF ₃	4-CF ₃	m. p. 144 °C
26	H	H	H	H	3-Cl	4-OCF ₃	4-OCF ₃	m. p. 130-131 °C
27	H	H	H	H	4-Cl	4-NO ₂	4-Cl	m. p. 162.2 °C
28	H	H	H	H	4-Cl	4-NO ₂	4-OCF ₃	m. p. 111.0-115.1 °C
29	H	H	H	H	3-F	4-CN	4-Cl	m. p. 154-156 °C
30	H	H	H	H	3-F	4-CN	4-CF ₃	m. p. 178 °C
31	H	H	H	H	3-F	4-CN	4-OCF ₃	m. p. 155.9-156.8 °C
32	H	H	H	H	3-CH ₃	4-CN	4-Cl	m. p. 127 °C
33	H	H	H	H	3-CH ₃	4-CN	4-CF ₃	m. p. 153-155 °C
34	H	H	H	H	3-CH ₃	4-CN	4-OCF ₃	m. p. 166 °C
35	H	H	H	H	4-CH ₃	4-Cl	4-CF ₃	m. p. 167.9-169.5 °C
36	H	H	H	H	4-CH ₃	4-Cl	4-OCF ₃	m. p. 167.4 °C
37	H	H	H	H	4-CH ₃	4-CN	4-OCF ₃	m. p. 150.6-151.2 °C
38	H	H	H	H	3-CF ₃	4-CN	4-Cl	m. p. 164-165 °C
39	H	H	H	H	3-CF ₃	4-CN	4-F	m. p. 173-175 °C
40	H	H	H	H	3-CF ₃	4-CN	4-Br	m. p. 164 °C
41	H	H	H	H	3-CF ₃	4-CN	4-I	m. p. 80 °C
42	H	H	H	H	3-CF ₃	4-CN	4-CF ₃	m. p. 191.5-192.0 °C

[Table 3]

第 1 表 (続 き)

No.	R ¹	R ²	R ³	R ⁴	(X) _l	(Y) _m	(Z) _n	物 性
43	H	H	H	H	3-CF ₃	4-CN	4-NO ₂	m. p. 236-238 °C
44	H	H	H	H	3-CF ₃	4-CN	4-CN	m. p. 174.5-175.1 °C
45	H	H	H	H	3-CF ₃	4-CN	3-CF ₃	m. p. 151.1-152.5 °C
46	H	H	H	H	3-CF ₃	4-CN	4-OCH ₃	m. p. 167 °C
47	H	H	H	H	3-CF ₃	4-CN	4-OCF ₃	m. p. 151.0 °C
48	H	H	H	H	3-CF ₃	4-CN	4-O- 	m. p. 156 °C
49	H	H	H	H	3-CF ₃	4-CN	2,4-Cl ₂	m. p. 78 °C
50	H	H	H	H	3-CF ₃	4-CN	3,4-Cl ₂	m. p. 213 °C
51	H	H	H	H	3-CF ₃	4-CN	3,5-Cl ₂	m. p. 169 °C
52	H	H	H	H	3-CF ₃	4-CN	3-Cl-4-F	m. p. 194 °C
53	H	H	H	H	3-CF ₃	4-CF ₃	4-CF ₃	m. p. 144.2 °C
54	H	H	H	H	3-CF ₃	4-CF ₃	4-OCF ₃	m. p. 142.6-144.7 °C
55	H	H	H	H	3-CF ₃	4-OCF ₃	4-Cl	m. p. 124 °C
56	H	H	H	H	3-CF ₃	4-OCF ₃	4-CF ₃	m. p. 108 °C
57	H	H	H	H	3-CF ₃	4-OCF ₃	4-OCF ₃	m. p. 105-106 °C
58	H	H	H	H	3-CF ₃	4-SCH ₃	4-Cl	m. p. 146 °C
59	H	H	H	H	3-CF ₃	4-SCH ₃	4-OCF ₃	m. p. 134 °C
60	H	H	H	H	3-CF ₃	4-SOCH ₃	4-OCF ₃	m. p. 171 °C
61	H	H	H	H	3-CF ₃	4-SO ₂ CH ₃	4-OCF ₃	m. p. 183-194 °C
62	H	H	H	H	3,4-Cl ₂	4-CN	4-CF ₃	m. p. 224-231 °C
63	H	H	H	H	3,4-Cl ₂	4-CN	4-OCF ₃	m. p. 224.0 °C

[Table 4]

第 1 表 (続き)

No.	R ¹	R ²	R ³	R ⁴	(X) _l	(Y) _m	(Z) _n	物 性
64	H	H	H	H	3,5-Cl ₂	4-CN	4-CF ₃	m. p. 255.5-258.0 °C
65	H	H	H	H	3,5-Cl ₂	4-CN	4-OCF ₃	m. p. 221.7-223.3 °C
66	H	CH ₃	H	H	4-Cl	4-Cl	4-Cl	ペースト状物
67	H	CH ₃	H	H	4-Cl	4-Cl	4-OCF ₃	ペースト状物
68	H	H	H	CH ₃	3-Cl	4-CN	4-OCF ₃	nD 1.5850 (25 °C)
69	H	H	H	CH ₃	4-Cl	4-Cl	H	nD 1.6365 (27 °C)
70	H	H	H	CH ₃	4-Cl	4-Cl	4-Cl	ペースト状物
71	H	H	H	CH ₃	4-Cl	4-Cl	4-OCF ₃	nD 1.5839 (27 °C)
72	H	H	CH ₃	H	3-CF ₃	4-CN	4-Cl	m. p. 209-211 °C
73	H	H	CH ₃	H	3-CF ₃	4-CN	4-CF ₃	m. p. 181 °C
74	H	H	H	H	3-CF ₃	4-SO ₂ CH ₃	4-Cl	m. p. 228 °C
75	H	H	H	H	3-CF ₃	4-SOCH ₃	4-Cl	m. p. 178 °C
76	H	H	H	H	3-CF ₃	4-CN	4-OSO ₂ CF ₃	m. p. 172 °C
77	H	H	H	H	3-CF ₃	4-CN	4-OCF ₃ CHF ₃	m. p. 153 °C
78	H	H	H	H	3-CF ₃	4-SCHF ₃	4-OCF ₃	m. p. 134 °C
79	H	H	H	H	3-CF ₃	4-SCHF ₃	4-Cl	m. p. 143 °C
80	H	H	H	H	3-CF ₃	4-SCHF ₃	4-Br	m. p. 145 °C
81	H	H	H	H	3-CF ₃	4-SOCHF ₃	4-OCF ₃	m. p. 143 °C
82	H	H	H	H	3-CF ₃	4-SOCHF ₃	4-Cl	m. p. 181 °C
83	H	H	H	H	3-CF ₃	4-SOCHF ₃	4-Br	m. p. 171 °C
84	H	H	H	H	3-CF ₃	4-SO ₂ CHF ₃	4-OCF ₃	m. p. 109-110 °C

[Table 5]

第 1 表 (続き)

No.	R ¹	R ²	R ³	R ⁴	(X) ₁	(Y) _m	(Z) _n	物 性
85	H	H	H	H	3-CF ₃	4-SO ₂ CHF ₂	4-Cl	m.p. 222 °C
86	H	H	H	H	3-CF ₃	4-SO ₂ CHF ₂	4-Br	m.p. 213 °C
87	H	H	H	H	3-NO ₂	4-CN	4-OCF ₃	m.p. 180-181 °C
88	H	H	H	H	3-NO ₂	4-CN	4-CF ₃	m.p. 213-215 °C
89	H	H	H	H	3-NO ₂	4-CN	4-Cl	m.p. 205 °C
90	H	H	H	H	3-NO ₂	4-CN	4-Br	m.p. 215-217 °C
91	H	H	H	H	3-C ₂ H ₅	4-CN	4-OCF ₃	m.p. 157 °C
92	H	H	H	H	3-C ₂ H ₅	4-CN	4-CF ₃	m.p. 166 °C
93	H	H	H	H	3-C ₂ H ₅	4-CN	4-Cl	m.p. 142 °C
94	H	H	H	H	3-C ₂ H ₅	4-CN	4-Br	m.p. 133 °C
95	H	H	H	H	3-OCF ₃	4-CN	4-OCF ₃	m.p. 154 °C
96	H	H	H	H	3-OCF ₃	4-CN	4-CF ₃	m.p. 157 °C
97	H	H	H	H	3-OCF ₃	4-CN	4-Cl	m.p. 168 °C
98	H	H	H	H	3-OCF ₃	4-CN	4-Br	m.p. 158 °C
99	H	H	H	H	4-CH ₃	4-CN	4-OCF ₃	m.p. 170 °C
100	H	H	H	H	4-CH ₃	4-CN	4-CF ₃	m.p. 160 °C
101	H	H	H	H	4-CH ₃	4-CN	4-Cl	m.p. 158 °C
102	H	H	H	H	4-CH ₃	4-CN	4-Br	m.p. 178 °C
103	H	H	H	H	4-Cl	4-CN	4-OCF ₃	m.p. 158 °C
104	H	H	H	H	4-Cl	4-CN	4-CF ₃	m.p. 168 °C
105	H	H	H	H	4-Cl	4-CN	4-Cl	m.p. 211 °C

[Table 6]

第 1 表 (続き)

No.	R ¹	R ²	R ³	R ⁴	(X) ₁	(Y) _m	(Z) _n	物 性
106	H	H	H	H	2-Cl	4-CN	4-OCF ₃	nD 1.5882(10°C)
107	H	H	H	H	3-Cl	2-CN	4-OCF ₃	m.p. 148 °C
108	H	H	H	H	4-F-3-Cl	4-CN	4-OCF ₃	m.p. 187-189 °C
109	H	H	H	H	4-F-3-Cl	4-CN	4-Cl	m.p. 184 °C
110	H	H	H	H	3-SCH ₃	4-CN	4-OCF ₃	m.p. 126 °C
111	H	H	H	H	3-SCH ₃	4-CN	4-Br	m.p. 162.6-163.1 °C
112	H	H	H	H	3-SOCH ₃	4-CN	4-OCF ₃	m.p. 179.0-181.6 °C
113	H	H	H	H	3-SOCH ₃	4-CN	4-Br	m.p. 129.8-130.6 °C
114	H	H	H	H	3-SO ₂ CH ₃	4-CN	4-OCF ₃	m.p. 212-214 °C
115	H	H	H	H	3-SO ₂ CH ₃	4-CN	4-Br	m.p. 199.5-200.1 °C
116	H	H	H	H	3-Cl	4-C=CH	4-OCF ₃	m.p. 173.8 °C

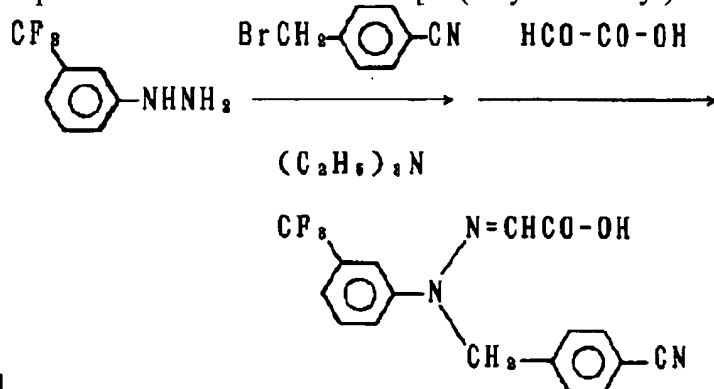
[0009] Physical properties show the NMR data of a paste-like object in the 2nd table among the 1st table.

第 2 表

No.	NMR (CDCl ₃ /TMS, δ 値(ppm))
70	1.82(3H, s), 4.72(2H, s), 6.73-7.80(12H, m), 8.95(1H, s).

Although the typical example of this invention is shown below, this invention is not limited to these.

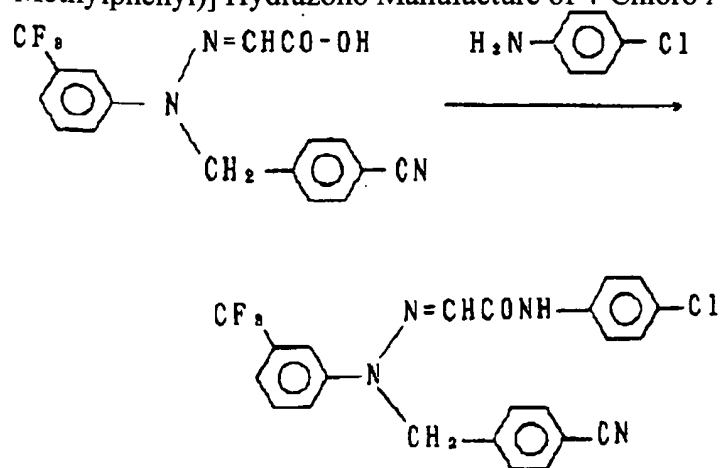
[0010] Example 11-1. Manufacture of a 2-[N-(4-cyano benzyl)-N-(3-trifluoro methylphenyl)] hydrazone



acetic acid

3-trifluoromethyl phenylhydrazine 13.46g (76.5 millimol) was dissolved in toluene 100ml, triethylamine 8.12g (80.4 millimol) and 4-cyano benzyl bromide 14.99g (76.5 millimol) were added, and it reacted to the bottom of 3-hour heating. After reaction termination, reaction mixture was rinsed (50mlx2), the organic layer was condensed, subsequently to ethanol 80ml the concentrate was dissolved, 11.51g (62.2 millimol) of glyoxylic-acid water solutions was dropped 40% at the bottom of ice-cooling, and stirring was performed to the bottom of a room temperature for 2 hours. The solvent was distilled out of the reaction solution containing the specified substance after reaction termination, 50ml of water was added, ethyl acetate (100mlx2) extracted, the extract was dried with anhydrous sodium sulfate, the crystal which condensed and deposited under reduced pressure was washed with hexane-ether mixed liquor, and the 13.02g specified substance was obtained.

Physical properties: m.p.220 degree C Yield 60.2% [0011] 1-2. 2-[N-(4-Cyano Benzyl)-N-(3-Trifluoro Methylphenyl)] Hydrazone Manufacture of 4-Chloro Acetanilide (Compound No.39)

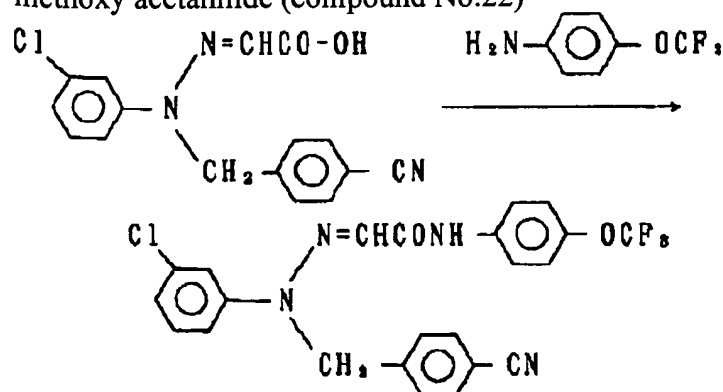


0.59g (1.7 millimol) of 2-[N-(4-cyano benzyl)-N-(3-trifluoro methylphenyl)] hydrazone acetic acids obtained by 1-1 was suspended in 7ml of carbon tetrachlorides, 0.40g (3.4 millimol) of thionyl chlorides

was added, and heating reflux was carried out for 1.5 hours. In addition to the solution which dissolved 4-chloroaniline 0.62g (1.7 millimol) and triethylamine 0.37g (3.7 millimol) for the acid chloride obtained by distilling off under reduced pressure of a reaction solvent in tetrahydrofuran 10ml, stirring was performed under the room temperature after reaction termination for 1 hour. After reaction termination, 10ml of water was added to reaction mixture, ethyl acetate (100mlx2) extracted the specified substance, the extract was dried with anhydrous sodium sulfate, and it condensed under reduced pressure. The obtained residue was refined by silica gel column chromatography - (hexane-ethyl acetate), and the 0.51g specified substance was obtained.

Physical properties m.p.164-165 degree C Yield 65.0%

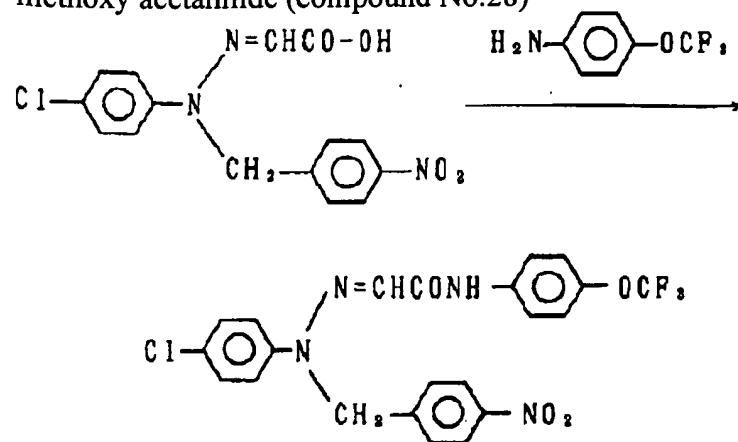
[0012] Example 2 2-[N-(3-chlorophenyl)-N-(4-cyano benzyl)] hydrazono Manufacture of 4-trifluoro methoxy acetanilide (compound No.22)



1.50g [of 2-[N-(3-chlorophenyl)-N-(4-cyano benzyl)] hydrazono acetic acids manufactured like 1-1] (4.8 millimol) and iodation 2-chloro-1-methyl pyridinium 1.34g (5.3 millimol) and 4-trifluoro methoxyaniline 0.85g (4.8 millimol) were dissolved in pyridine 20ml, and heating reflux was carried out for 3 hours. The solvent was distilled off after reaction termination, 30ml of water was added, ethyl acetate (50mlx2) extracted the specified substance, the extract was dried with anhydrous sodium sulfate, and it condensed under reduced pressure. The obtained residue was refined by silica gel column chromatography - (hexane-ethyl acetate), and the 1.64g specified substance was obtained.

Physical properties m.p.160.5-162.0 degree C Yield 72.3%

[0013] Example 3 2-[N-(4-chlorophenyl)-N-(4-nitrobenzyl)] hydrazono Manufacture of 4-trifluoro methoxy acetanilide (compound No.28)

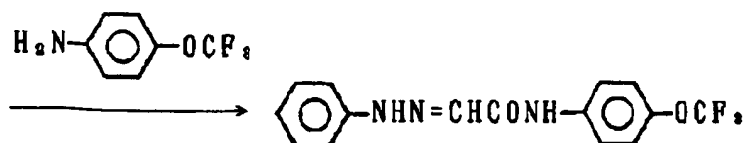
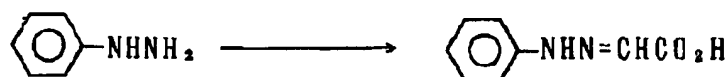
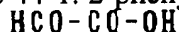


1.30g [of 2-[N-(4-chlorophenyl)-N-(4-nitrobenzyl)] hydrazono acetic acids] (3.9 millimol) and carbonyldiimidazole 0.63g (3.9 millimol) manufactured like 1-1 was dissolved in tetrahydrofuran 10ml, and stirring was performed to the bottom of a room temperature for 5 hours. After reaction termination, 30ml of water was added, ethyl acetate (50mlx2) extracted, the extract was dried with anhydrous sodium

sulfate, the residue condensed and obtained under reduced pressure was dissolved in pyridine 20ml, 4-trifluoro methoxyaniline 0.69g (3.9 millimol) and 4-dimethylaminopyridine 0.10g (0.8 millimol) were added, and it stirred under 12-hour heating reflux. After reaction termination, the solvent was distilled off, 30ml of water was added, ethyl acetate (50mlx2) extracted the specified substance, the extract was dried with anhydrous sodium sulfate, the residue condensed and obtained under reduced pressure was refined by silica gel column chromatography - (hexane-ethyl acetate), and the 0.95g specified substance was obtained.

Physical properties m.p.111.0-115.1 degree C Yield 49.5%

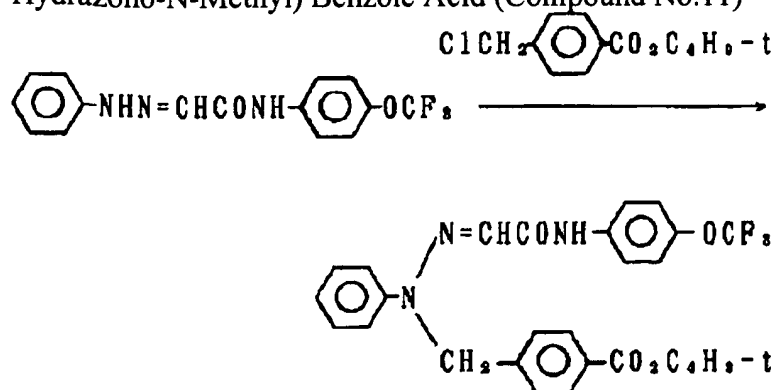
[0014] Example 44-1. 2-phenyl hydrazono Manufacture of 4-trifluoro methoxy acetanilide



Phenylhydrazine 30.24g (0.28 mols) was dissolved in ethanol 200ml, 51.80g (0.28 mols) of glyoxylic-acid water solutions was dropped 40% at the bottom of ice-cooling, and it stirred under the room temperature for 2 hours. 20.2g of phenyl hydrazono acetic acids was obtained after reaction termination by washing the crystal which distilled off and deposited under reduced pressure of a solvent with hexane-ether mixed liquor (yield 43.9%). The solution which dissolved obtained 7.81g [of phenyl hydrazono acetic acids] (47.6 millimol) and triethylamine 10.58g (104.7 millimol) in dichloromethane 30ml was dropped at the solution which dissolved iodation 2-chloro-1-methyl pyridinium 12.17g (47.6 millimol) and 4-trifluoro methoxyaniline 8.43g (47.6 millimol) in dichloromethane 100ml, and stirring was performed to the bottom of a room temperature for 5 hours. After reaction termination, the solvent was distilled off, 50ml of water was added, ethyl acetate (100mlx2) extracted the specified substance, the extract was dried with anhydrous sodium sulfate, and it condensed under reduced pressure, and the obtained residue was refined by silica gel column chromatography - (hexane-ethyl acetate), and the 7.62g specified substance was obtained.

Physical properties m.p.151.2-154.3 degree C Yield 49.6%

[0015] 4-2. Tert-Butyl Manufacture of 4-[2-(4-Trifluoro Methoxypheny Carbamoyl Methyl-N-Phenyl Hydrazono-N-Methyl) Benzoic Acid (Compound No.11)



Phenyl hydrazono obtained by 4-1 4-trifluoro methoxy acetanilide 0.71g (2.2 millimol) is dissolved in dimethylformamide 20ml, and it is Potassium tert under ice-cooling. - Butoxide 0.27g (2.4 millimol) and tert - Butyl 0.54g of 4-chloro methyl benzoic acids was added, and the reaction was performed to the bottom of a room temperature for 3 hours. After reaction termination, 50ml of iced water was added,

ethyl acetate (100mlx2) extracted the specified substance, the extract was dried with anhydrous sodium sulfate, the residue condensed and obtained under reduced pressure was refined by silica gel column chromatography - (hexane-ethyl acetate), and the 0.70g specified substance was obtained.

Physical properties m.p.142.2-143.7 degree C Yield 70.0%

[0016] General formula of this invention (I) The insecticide for plantation arts which makes an active principle the hydrazone derivative expressed Paddy rice, Alike and suitable for insect pest control, such as various agriculture and forestry which injure crops, a flowering plant, etc. of vegetables, a fruit tree, and others, horticulture, a stored product insect, and a medically important insect or a nematode For example, apple Adoxophyes (adoxophyes orana fasciata), Smaller tea tortrix, Adoxyphyles sp. (Adoxyphyles sp.), apple KOSHINKUI (Grapholita inopinata), A NASHIHIME codling moth (Grapholita mlestia), a soybean pod borer (Leguminivora glycinivorella), Mulberry HAMAKI (Olethreutes mori), Caloptilia theivora (Caloptilia thevivora), Apple HOSOGA (Caloptilia zachrysa), Phyllonorycter ringoniella (Phyllonorycterringoniella), NASHIHOSOGA (Spulerina astaurota), a cabbage butterfly (Pie-rs rapae crucivora), Helicoverpa armigera (Heliothis sp.), KODORINGA (L-aspeyresia pomonella), A cabbage moth (Plutella xylostella), apple HIMESHINKUI (Argyresthia conjugella), A peach codling moth (Carposina niponensis), Chilo (Chilo suppressalis), Cnaphalocrocis medinalis (Cnaphalocrocis medinalis), Tea MADARAMEIGA (Ephestia elutella), mulberry NOMEIGA (Glyphodes pyloa-lis), SANKAMEIGA (Scirpophaga incertulas), ICHIMONJISESERI (Parna-ra guttata), Leucania (Pseudaletia separata), A rice armyworm (Sesamia i-nferens), a tobacco cutworm (Spodoptera litura), Lepidoptera noxious insects, such as SHIROICHIMONJIYOTOU (Spodoptera exigua), A free-wheel-plate ten leafhopper (Macrostes fasci-frons), Nephrotettix (Nephrotettix cincticeps), A rice brown planthopper (N-ilaparvata lugens), Sogatella furcifera (Sogatella furcifera), A mandarin orange jumping plant lice (Diaphorina citri), a grape white fly (Aleurolobus taonabae), A tobacco white fly (Bemisia tabaci), an ONSHITSU white fly (Trialeurodes vaporari-orum), A fake Japanese radish aphid (Lipaphis erysimi), a green peach aphid (Myzus persicae), TSUNOROMUSHI (Ceroplastes ceriferus), A mandarin orange cotton scale insect (Pulvinaria aurantii), A mandarin orange mull scale insect (Pseudaonidiaduplex), A pear mull scale insect (Comstockaspis perniciosus), Hemiptera noxious insects, such as an Arrowhead scale (Unaspis yanonensis), A meadow nematode (Pratylenchus sp.), a soybean beetle (Anomala rufocuprea), A Japanese beetle (Popillia japonica), a cigarette beetle (Lasioderma serricorne), A powder-post beetle (Lyctus brunneus), a NIJUUYAHOSHI ten tow (Epilachna vigintioctopu-nectata), Callosobruchus (Callosobruchus chinensis), A YASAI weevil (L-istroderes costirostris), A rice weevil (Sitophilus zeamais), a boll weevil (Anthonomus grandis grandis), A rice Ms. weevil (Lissorhoptrus oryzophilus), Aulacophora femoralis (Aulacophora femoralis), rice DOROOIMUSHI (O-ulema oryzae), A turnip fly (Phyllotreta striolata), A rice weevil (Sitophilus zeamais), MATSUNO woodengraver (Tomicus piniperda), A Colorado POTETOBİ-torr (Leptinotarsa decemlineata), A MEKISHIKAMBI-MBI-torr (Epilachna varivestis), Coleoptera noxious insects, such as cone root worms (Diabrotica sp.), A melon fruit fly (Dacus (Zeugodacus) cucurbitae), An oriental fruit fly (Dacus (Bactrocera) dorsalis), Agromyza oryzae (Agromyza oryzae), an onion fly (Delia antiqua), A seed-corn fly (Delia platura), soybean SAYATAMABAE (Asphondylia sp.), Diptera noxious insects, such as a muscid (Musca domestica) and a red house mosquito (Culex pipiens pipiens), A MINAMI meadow nematode (Pratylenchus coffeae), Potato cyst SENCHUU (Globodera rostochiensis), A root-knot nematode (Meloidogyne sp.), mandarin orange NESENCHUU (Tylenchulus semipenetrans), A fake meadow nematode (Aphelenchus avenae), It has the insect-killing effectiveness also to the Tylenchida noxious insects, such as HAGARESENCHUU (Aphelenchoides ritzemabosi), etc., and has remarkable effectiveness to noxious insects, such as Lepidoptera and Coleoptera, especially. In addition, a scientific name etc. is based on an agriculture-and-forestry noxious animal and insect directory 1987 edition (volume on Japanese application animal entomology meeting).

[0017] Since the insecticide for plantation arts of this invention has the remarkable insect-killing effectiveness to said noxious insect or medically important insect which injures crops, a flowering plant, etc. of a paddy field, a fruit tree, vegetables, and others When generating is checked, according to the stage when generating of noxious insects is predicted, the generating front stirrup of noxious insects A

paddy field, If medically important insects, such as paddy field water, such as a fruit tree, vegetables, other crops, and a flowering plant, forage, or soil, have, the expected effectiveness of the insecticide of this invention is done so by processing into the slot around the house in the house where generating or generating of the above-mentioned noxious insect which injures men and beasts is predicted etc.

However, this invention is not limited only to these modes. General formula of this invention (I) When using the hydrazone derivative expressed as an insecticide for plantation arts, it is common to manufacture medicine and use it for a configuration with sufficient convenience on use according to the conventional method on agricultural-chemicals pharmaceutical preparation. namely, general formula (I) of this invention the hydrazone derivative expressed -- these -- a suitable inert carrier -- or what is necessary is just to use it for proper dosage forms, for example, suspension, an emulsion, liquids and solutions, water dispersible powder, a granule, powder material, a tablet, etc., accepting the need, making it blend and mix, sink in, adsorb or adhere to an adjuvant and a rate suitable together, and manufacturing medicine [dissolution, separation and] As an ingredient which may be any of a solid-state or a liquid as an inert carrier which can be used by this invention, and can become solid support For example, soybean powder, grain powder, wood flour, bark powder, sawdust, tobacco caulome powder, walnut shell powder, Synthetic polymers, such as wheat bran, fibrin powder, residue after a vegetable extractives extract, and grinding synthetic resin, Clay, talc (for example, a kaolin, a bentonite, acid clay, etc.) (for example, talc, PIROFIRAIDO, etc.), and silicas (for example, with the synthetic quantity distribution silicic acid called diatomaceous earth, silica sand, a mica, white carbon [water fines silicon, and water silicic acid) there are some which contain a calcium silicate as a principal component with a product.] Chemical fertilizer, such as inorganic mineral powder, such as activated carbon, sulfur powder, a pumice, baking diatomaceous earth, a brick grinding object, fly ash, sand, a calcium carbonate, and calcium phosphate, an ammonium sulfate, ammonium phosphate, an ammonium nitrate, a urea, and an ammonium chloride, a compost, etc. can be mentioned, and these are independent or are used in the form of two or more sorts of mixture.

[0018] Although it has solvent ability in itself and the support which it does not have others and solvent ability, is chosen from what ** will also make distribute an active principle compound and will deal in it with the help of an adjuvant, for example, is listed to a degree as an example of representation can be illustrated as an ingredient which can become the support of a liquid These are independent or are used in the form of two or more sorts of mixture. For example, water, alcohols (for example, a methanol, ethanol, and isopropanol --) ketones (for example, an acetone --), such as a butanol and ethylene glycol A methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, ether (for example, ethyl ether and dioxane --), such as a cyclohexanone aliphatic hydrocarbon (for example, kerosine --), such as cellosolve, dipropyl ether, and a tetrahydrofuran aromatic hydrocarbon (for example, benzene, toluene, and a xylene --), such as mineral oil halogenated hydrocarbon (for example, a dichloroethane --), such as solvent naphtha and alkyl naphthalene ester (for example, ethyl acetate --), such as chloroform, a carbon tetrachloride, and chlorination benzene JISOPU pill phthalate, dibutyl phthalate, JOKURU phthalate, etc. can mention amides (for example, dimethylformamide, a diethyl formamide, dimethylacetamide, etc.), nitril, and dimethyl sulfoxide (for example, acetonitrile etc.). It is also possible to be able to raise the typical adjuvant illustrated next as other adjuvants, and for these adjuvants to be used according to the purpose, and to be independent, and to use together two or more sorts of adjuvants in a certain case, and not to use an adjuvant at all in a certain case.

[0019] A surface active agent is used for emulsification of an active principle compound, distribution, solubilization, and/or the humid purpose, for example, surface active agents, such as polyoxyethylene alkyl ether, polyoxyethylene alkyl aryl ether, polyoxyethylene higher-fatty-acid ester, polyoxyethylene resin acid ester, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monooleate, alkylaryl sulfonates, a naphthalene sulfonic-acid condensate, a ligninsulfonic acid salt, and a higher-alcohol sulfate, can be illustrated. Moreover, for the purpose of distributed stabilization of an active principle compound, adhesion, and/or association, the adjuvant illustrated next can also be used, for example, adjuvants, such as casein, gelatin, starch, methyl cellulose, a carboxymethyl cellulose, gum arabic, polyvinyl alcohol, dry distilled wood turpentine, rice-bran oil, a bentonite, and a ligninsulfonic acid salt,

can also be used. The adjuvant listed to a degree for fluid amelioration of a solid-state product can also be used, for example, adjuvants, such as a wax, a stearate, and phosphoric acid alkyl ester, can be used. As a deflocculant of a suspensibility product, adjuvants, such as for example, a naphthalene sulfonic-acid condensate and condensed phosphate, can also be used. As a defoaming agent, adjuvants, such as silicon oil, can also be used, for example.

[0020] When it can adjust if needed, for example, it considers as powder material or a granule and the blending ratio of coal of an active principle compound considers as 0.01 - 50 % of the weight and an emulsion, or water dispersible powder, 0.01 - 50 % of the weight is suitable for it similarly. general formula (I) of this invention in order that the insecticide for plantation arts which makes an active principle the hydrazone derivative expressed may prevent various noxious insects -- as it is -- or an amount effective in insect pest control in the form which diluted suitably with water etc. or was made to suspend -- the noxious insect concerned -- or generating or growth of the noxious insect concerned should just use it for the location which is not desirable, applying. General formula of this invention (I) What is necessary is just to choose it from the range of 0.1g - 5kg per 10a. suitably according to the purpose as an active principle compound, although the amount of the insecticide for plantation arts used which makes an active principle the hydrazone derivative express is change by various factors, for example, the purpose, an object noxious insect, the growth situation of crops, the generating inclination of a noxious insect, the weather, an environmental condition, the pharmaceutical form, the use approach, the use location, a use stage, etc. General formula of this invention (I) It is also possible to use further the insecticide for plantation arts which makes an active principle the hydrazone derivative expressed for the purpose for expansion of a noxious insect for prevention and ***** term which aims at reduction of a dose, mixing with other insecticides or a germicide. Although the typical example of a formula and the example of a trial of this invention are shown below, this invention is not limited to these. In addition, that it is with the section shows the weight section among the example of a formula.

[0021] Example 1 of a formula This invention compound The 50 sections Xylene The 40 sections Polyoxyethylene nonyl phenyl ether Mixture with alkylbenzene-sulfonic-acid calcium Carry out the mixed dissolution and let the 10 or more sections be an emulsion at homogeneity.

Example 2 of a formula This invention compound The three sections Clay powder The 82 sections Diatomaceous earth powder Preferential grinding of the 15 or more sections is carried out to homogeneity, and it considers as powder material.

Example 3 of a formula This invention compound The five sections Mixed powder of a bentonite and clay The 90 sections Ligninsulfonic acid calcium The 5 or more sections are mixed to homogeneity, and it kneads moreover, and it corns and dries and let the water of optimum dose be a granule.

Example 4 of a formula This invention compound The 20 sections A kaolin and synthetic quantity distribution silicic acid The 75 sections Polyoxyethylene nonyl phenyl ether and Al Mixture with kill benzenesulfonic acid calcium Preferential grinding of the 5 or more sections is carried out to homogeneity, and it considers as water dispersible powder.

[0022] Example 1 of a trial Tobacco cutworm (*Spodoptera litura*) It is 500 ppm about the drugs which make an active principle the insecticidal test this invention compound to receive. The cabbage folia (form: *Brassica oleracea*) was immersed in the diluted drug solution for about 30 seconds. After putting into the plastics petri dish with a diameter of 9cm and inoculating a tobacco cutworm second instar larva after an air dried, it covered and put on 25-degree-C thermostatic chamber gently. The number of life-and-death insects was investigated eight days after inoculation, mortality was computed by the following formula, and it judged in accordance with the following criteria.

The 1st division ten-animal 3 ream system [a formula 1]

$$\text{補正死虫率 (\%)} = \frac{\text{死虫数}}{\text{接種虫数}} \times 100$$

Criterion

A [... 79% - 50% result of mortality is shown in the 3rd table.] ... Mortality 100%B ... 99% - 90% of

mortality C ... 89% - 80% of mortality D

[0023]

第 3 表

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
3	500	C	31	500	A
4	500	A	32	500	A
5	500	A	33	500	A
7	500	D	34	500	A
8	500	D	38	500	A
9	500	A	40	500	A
10	500	A	41	500	A
11	500	C	47	500	A
14	500	A	53	500	A
17	500	A	54	500	A
18	500	A	64	500	D
19	500	A	65	500	C
20	500	A	73	500	A
21	500	A	76	500	A
22	500	A	77	500	A
23	500	D	78	500	A
25	500	A	79	500	A
26	500	A	80	500	A
27	500	C	81	500	A
28	500	A	83	500	C
29	500	A	84	500	A
30	500	A	87	500	A

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
88	500	D	104	500	A
89	500	D	108	500	A
91	500	C	110	500	A
94	500	D	111	500	D
95	500	D	112	500	A
100	500	A	113	500	D
102	500	D	115	500	D
103	500	A	116	500	A

[0024] example 2 of a trial substance -- the drugs which make an active principle the insecticidal test

this invention compound to an elephant (*Sitophilus zeamais*) imago -- 200 ppm Brown rice was immersed in the diluted drug solution for about 30 seconds. after an air dried -- a glass petri dish with a diameter of 4cm -- putting in -- substance -- after inoculating an elephant imago, it covered and put on 25-degree-C thermostatic chamber gently. The number of life-and-death insects was investigated eight days after inoculation, mortality was computed according to the example 1 of a trial, and it judged in accordance with the criteria of the example 1 of a trial. The 1st division ten-animal 3 ream system. A result is shown in the 4th table.

[0024]

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
4	200	D	9	200	D
7	200	B	17	200	B
8	200	C	18	200	C

第 4 表 (続き)

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
19	200	C	64	200	A
20	200	C	65	200	A
21	200	A	72	200	C
22	200	A	73	200	A
27	200	D	75	200	A
28	200	C	76	200	A
30	200	A	77	200	A
31	200	D	78	200	A
38	200	A	79	200	A
39	200	A	80	200	A
40	200	A	81	200	A
41	200	A	82	200	A
42	200	A	83	200	A
43	200	D	84	200	A
47	200	A	85	200	A
50	200	B	86	200	D
53	200	A	87	200	A
54	200	A	88	200	A
55	200	A	89	200	A
56	200	A	90	200	A
57	200	A	91	200	A
62	200	D	92	200	A
63	200	B	93	200	A

第 4 表 (続き)

No.	濃 度 (ppm)	判 定	No.	濃 度 (ppm)	判 定
94	200	A	106	200	A
95	200	A	107	200	A
96	200	A	108	200	A
97	200	D	109	200	A
98	200	A	110	200	A
100	200	A	111	200	A
101	200	A	112	200	A
102	200	A	113	200	A
103	200	A	114	200	A
104	200	A	115	200	A
105	200	A	116	200	A

[Translation done.]